

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : A01N 27/00, 43/00, 61/00, A61K 31/00, 31/01, 31/70		A1	(11) International Publication Number: WO 96/17517 (43) International Publication Date: 13 June 1996 (13.06.96)
(21) International Application Number: PCT/US95/15984		(74) Agents: FREELAND, Ralph, L., Jr. et al.; Burns, Doane, Swecker & Mathis, P.O. Box 1404, Alexandria, VA 22313-1404 (US).	
(22) International Filing Date: 8 December 1995 (08.12.95)		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, LS, MW, SD, SZ, UG).	
(30) Priority Data: 08/353,533 9 December 1994 (09.12.94) US		(71) Applicant (<i>for all designated States except US</i>): CHEVRON U.S.A. INC. [US/US]; 555 Market Street, San Francisco, CA 94105 (US).	
(60) Parent Application or Grant (63) Related by Continuation US Filed on 08/353,533 (CIP) 9 December 1994 (09.12.94)		(72) Inventors; and (75) Inventors/Applicants (<i>for US only</i>): OKAZAKI, Mark, E. [US/US]; 1256 Stirling Drive, Rodeo, CA 94572 (US). CHAN, Jim, H. [US/US]; 5331 Alhambra Valley Road, Martinez, CA 94533 (US). ABERNATHY, Susan, M. [US/US]; 166 Dunham Court, Hercules, CA 94547 (US). D'SOUZA, Adrian [CA/US]; 2008 Stratton Road, Walnut Creek, CA 94598 (US).	
Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>			

(54) Title: HYDRAULIC FLUIDS FOR USE IN AIRCRAFT

(57) Abstract

Disclosed is an aircraft hydraulic fluid comprising a novel combination of additives and organic phosphate basestocks which provides excellent results in scavenging acid generated by the partial esters of phosphoric acid, in controlling erosion in the formulation and in reducing electrodeposited solids.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LJ	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Larvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

HYDRAULIC FLUIDS FOR USE IN AIRCRAFT

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to novel hydraulic fluids containing a specific combination of components which combination imparts beneficial properties to the fluid, particularly when used as aircraft hydraulic fluids.

5 State of the Art

Hydraulic fluids, including those based on organic phosphate esters, are well known in the art and have been recognized for quite some time as advantageous for use in aircraft where they operate as a power transmission medium. In addition to the organic phosphate ester basestock, the aircraft 10 hydraulic fluid is conventionally formulated to include additives such as viscosity index improvers, anti-erosion agents, acid scavengers, anti-oxidants, rust inhibitors and the like so that the composition meets the needs of modern aircraft.

One problem typically encountered with aircraft hydraulic fluids is 15 that combinations of additives in a particular basestock do not always provide for the desired or expected combination of properties. For example, a combination of additives in one basestock may not perform nearly as well as in another basestock. Also, the inclusion of an additional additive into a hydraulic fluid formulation can deleteriously affect the 20 performance of one or more of the additives already employed in that formulation. The art has typically assigned some sort of incompatibility of the basestock with one or more of the additives employed in conjunction therewith or incompatibility of one additive with one or more of the other additives used in the formulation in order to explain this phenomena. In

-- 2 --

any event, formulation of suitable aircraft hydraulic fluids is an empirical exercise and the formulator typically is required to balance the properties of the formulation against the particular additives and basestocks employed.

Particular problems of concern to the formulator include the

5 inclusion of suitable acid scavengers, anti-erosion agents and viscosity index improvers in the aircraft hydraulic formulation. Specifically, in use, aircraft hydraulic fluids commonly become contaminated with moisture. Water enters the hydraulic system with air bled from an engine compressor stage. During operation, the moisture level in the fluid can typically range
10 from about 0.1 to about 0.5 weight percent. Water causes hydrolytic decomposition of phosphate esters to produce partial esters of phosphoric acid which can cause corrosion. In turn, corrosion can lead to the presence of metallic or other insoluble components which may result in filter clogging thereby necessitating filter replacement. The presence of metallic
15 or other insoluble components can also cause a change in the physical and chemical properties of the fluid, thereby requiring premature draining of the fluid from the system. Hydrolytic breakdown of the ester is accelerated if the water content exceeds about 0.5 weight percent and by the presence of partial esters of phosphoric acid. Accordingly, phosphate
20 ester aircraft hydraulic fluids are conventionally formulated to contain an acid scavenger which neutralizes partial esters of phosphoric acid released by this hydrolytic breakdown.

Similarly, an anti-erosion agent is incorporated into the aircraft hydraulic fluid to counteract erosive conditions typically occurring in the
25 power transmission mechanisms of the aircraft. Erosion is a form of electrochemical corrosion, more precisely referred to as zeta corrosion. The process of erosion results in the wearing of the metering edges of the hydraulic valves leading to degraded performance of the hydraulic systems. Erosion can also lead to metal contaminants, in ionic form, which reduce
30 the oxidative stability of the fluid thereby accelerating corrosion and

-- 3 --

catalytically accelerating the decomposition of the phosphate ester basestock.

Viscosity index improvers are employed to limit the effect of temperature on the viscosity of the hydraulic fluid composition.

5 Specifically, while viscosity control at both elevated and reduced temperatures is essential for the hydraulic fluid, it is critically important that viscosity control be maintained at reduced temperatures typically encountered during flights at high altitudes.

It is recognized in the art that not all combinations of phosphate 10 ester basestocks, acid scavengers, erosion inhibitors and viscosity index improvers are compatible with each other. Accordingly, it would be particularly desirable to provide for an aircraft hydraulic fluid comprising a phosphate ester basestock and as additives therein an acid scavenger, an anti-erosion agent and a viscosity index improver that are not incompatible 15 with each other or with the basestock and which function suitably under all conditions.

This invention overcomes the problems of the prior art by providing 20 for an aircraft hydraulic fluid comprising a novel combination of additives and organic phosphate basestocks which provides excellent results in scavenging acid generated by the partial esters of phosphoric acid, in controlling erosion at the metering edges of the hydraulic servo valves, in reducing electrodeposited solids and in maintaining suitable viscosity over a wide range of temperatures. These results are particularly surprising because rather than being incompatible, the additives and basestock 25 employed in the formulation described herein are, in fact, synergistic.

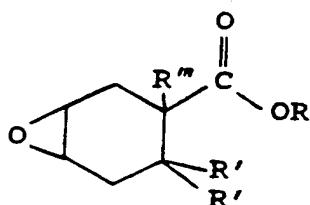
The formulation discovered by this invention comprises:

a basestock combination of from about 60 to 95 weight percent of a trialkyl phosphate and from about 5 to about 40 weight percent of a second component selected from the group consisting of a triaryl phosphate, a 30 mixture of a triaryl phosphate and a linear polyoxyalkylene material, and a

-- 4 --

linear polyoxyalkylene material which basestock is free of dialkyl aryl phosphate and alkyl diaryl phosphate,
an acid scavenger of the formula

5



10

15

20

25

30

where R is selected from the group consisting of an alkyl group of from 1 to 10 carbon atoms optionally containing from 1 to 4 ether oxygen atoms therein and cycloalkyl of from 3 to 10 carbon atoms, each R' is independently selected from the group consisting of hydrogen, alkyl of from 1 to 10 carbon atoms and -C(O)OR" where R" is alkyl of from 1 to 10 carbon atoms optionally containing from 1 to 4 ether oxygen atoms therein or cycloalkyl of from 3 to 10 carbon atoms, and R'' is selected from the group consisting of hydrogen, alkyl of from 1 to 10 carbon atoms and -C(O)OR" where R" is alkyl of from 1 to 10 carbon atoms optionally containing from 1 to 4 ether oxygen atoms therein or cycloalkyl of from 3 to 10 carbon atoms;

an anti-erosion agent which is a salt of perfluoroalkyl or perfluorocycloalkyl sulfonate;

and from about 1 to about 8 weight percent of a viscosity index improver to reduce the effect of temperature on viscosity by providing for a hydraulic fluid composition containing the VI improver and having a

viscosity of from about 3 to about 4 cSt at 210°F, a viscosity of from about 9 to about 12.5 cSt at 100°F, and a viscosity of less than about 2000 cSt at -65°F with the proviso that the viscosity index improver is not a poly(alkyl acrylate) ester.

While each of the components employed herein are similar to those heretofore disclosed for use in aircraft hydraulic fluids, the particular

-- 5 --

combination of these components is believed to be novel and unexpectedly leads to a balanced formulation providing synergistic results including, by way of example, reductions in electrodeposited solids, enhanced hydrolytic stability and/or improved erosion control while maintaining suitable viscosity over a wide range of temperatures. It is understood that not all formulations of this invention will necessarily provide all of the above synergies but each formulation will provide at least one of the above synergies.

In regard to the above, the use of a phosphate basestock comprising
10 a mixture of triaryl phosphate and trialkyl phosphate in aircraft hydraulic
fluids is disclosed in U.S. Patent No. 5,035,824; the use of alkali (e.g.,
potassium) perfluoroalkyl or perfluorocycloalkyl sulfonate as an anti-
erosion agent in aircraft hydraulic fluids is disclosed in U.S. Patent No.
3,679,587; and the use of certain epoxides of the formula described above
15 in aircraft hydraulic fluids is disclosed in U.S. Patent No. 3,723,320.
Moreover, commercially available hydraulic fluids used in aircraft and sold
under the trademark Skydrol® by Monsanto Company (St. Louis, Missouri,
USA) are believed to comprise a basestock having trialkyl phosphate,
20 dialkyl aryl phosphate and alkyl diaryl phosphate components with little or
no triaryl phosphate as well as potassium perfluorocyclohexyl sulfonate and
the monoepoxide 7-oxabicyclo[4.1.0]heptane-3-carboxylic acid, 2-
ethylhexyl ester.

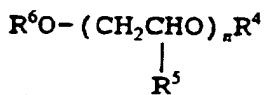
SUMMARY OF THE INVENTION

This invention is directed to an aircraft hydraulic fluid comprising a
25 novel combination of additives and organic phosphate basestocks which
provides excellent results in scavenging acid generated by the partial esters
of phosphoric acid, in controlling erosion in the formulation, and in
reducing electrodeposited solids. These results are particularly surprising
because rather than being incompatible, the additives and basestock
30 employed in the formulation described herein are, in fact, synergistic.

-- 6 --

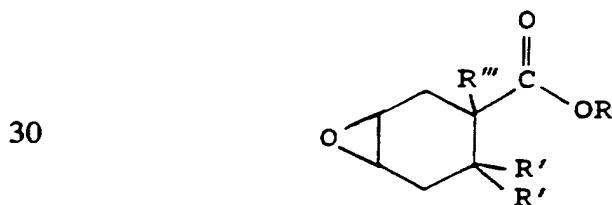
Specifically, in one of its composition aspects, this invention is directed to an aircraft hydraulic fluid comprising

- (a) from about 60 to about 90 weight percent, based on the total weight of the fluid, of an organic phosphate ester basestock wherein said organic phosphate ester basestock comprises from about 60 to 95 weight percent, based on the weight of the basestock, of a trialkyl phosphate wherein each of the alkyl groups thereof is independently from 1 to 12 carbon atoms and from about 5 to about 40 weight percent, based on the weight of the basestock, of a second component selected from the group consisting of a triaryl phosphate, a mixture of a triaryl phosphate and a linear polyoxyalkylene material, and a linear polyoxyalkylene material which basestock is free of dialkyl aryl phosphate and alkyl diaryl phosphate wherein each of the aryl groups of the triarylphosphate is independently phenyl or alkyl substituted phenyl having from 7 to 20 carbon atoms and still further wherein the linear polyoxyalkylene material is of the formula



wherein R^4 and R^6 are independently selected from the group consisting of hydrogen and hydrocarbyl groups of from 1 to about 30 carbon atoms, R^5 is selected from the group consisting of hydrogen and methyl, and n is an integer such that the number average molecular weight of the polymer is from about 300 to about 1000;

- (b) from about 4 to about 10 weight percent, based on the total weight of the hydraulic fluid, of an acid scavenger of the formula



where R is selected from the group consisting of an alkyl group of from 1 to 10 carbon atoms optionally containing from 1 to 4 ether oxygen

-- 7 --

- atoms therein and cycloalkyl of from 3 to 10 carbon atoms, each R' is independently selected from the group consisting of hydrogen, alkyl of from 1 to 10 carbon atoms and -C(O)OR" where R" is alkyl of from 1 to 10 carbon atoms optionally containing from 1 to 4 ether oxygen atoms
- 5 therein or cycloalkyl of from 3 to 10 carbon atoms, and R"" is selected from the group consisting of hydrogen, alkyl of from 1 to 10 carbons atoms and -C(O)OR" where R" is alkyl of from 1 to 10 carbon atoms optionally containing from 1 to 4 ether oxygen atoms therein or cycloalkyl of from 3 to 10 carbon atoms;
- 10 (c) from about 0.01 to about 0.1 weight percent, based on the total weight of the hydraulic fluid, of an anti-erosion agent which is a salt of perfluoroalkyl sulfonate or a perfluorocycloalkyl sulfonate wherein alkyl is alkyl of from 1 to 10 carbon atoms and cycloalkyl is cycloalkyl of from 3 to 10 carbon atoms; and
- 15 (d) from about 1 to about 8 weight percent of a viscosity index improver effective in reducing the effect of temperature on viscosity on the fluid by providing for a hydraulic fluid composition containing the VI improver which has a viscosity of from about 3 to about 4 cSt at 210°F, a viscosity of from about 9 to about 12.5 cSt at 100°F, and a viscosity of
- 20 less than about 2000 cSt at -65°F, with the proviso that the viscosity index improver is not a poly(alkyl acrylate) ester.
- In a preferred embodiment, the acid scavenger is selected from the group consisting of 7-oxabicyclo[4.1.0]heptane-3-carboxylic acid, 2-ethylhexyl ester and 7-oxabicyclo[4.1.0]heptane-3,4-dicarboxylic acid,
- 25 di(iso-butyl) ester.
- In another preferred embodiment, the aircraft hydraulic fluid described above further comprises
- (e) an effective amount of an anti-oxidant or mixture of anti-oxidants to inhibit oxidation of the hydraulic fluid, and
- 30 (f) an effective amount of a rust inhibitor or mixture of rust inhibitors.

-- 8 --

In another of its composition aspects, this invention is directed to an aircraft hydraulic fluid comprising

- (a) from about 70 to 80 weight percent, based on the total weight of the fluid, of tributyl phosphate, and from about 8 to 14 weight percent, 5 based on the total weight of the fluid, of tri(iso-propylphenyl)phosphate,
 - (b) from about 4.5 to about 7.5 weight percent, based on the total weight of the hydraulic fluid, of an acid scavenger which is the monoepoxide 7-oxabicyclo[4.1.0]heptane-3-carboxylic acid, 2-ethylhexyl ester,
 - 10 (c) from about 0.01 to about 0.1 weight percent, based on the total weight of the hydraulic fluid, of an anti-erosion agent which is a salt of perfluorocyclohexyl sulfonate,
 - (d) from about 0.5 to about 2 weight percent, based on the total weight of the hydraulic fluid, of an anti-oxidant or mixture of anti-oxidants,
 - 15 (e) from about 0.01 to about 0.5 weight percent, based on the total weight of the hydraulic fluid, of a rust inhibitor or mixture of rust inhibitors, and
 - (f) from about 1 to about 8 weight percent, based on the total weight of the hydraulic fluid, of a viscosity index improver effective in 20 reducing the effect of temperature on viscosity on the fluid by providing for a hydraulic fluid composition containing the VI improver which has a viscosity of from about 3 to about 4 cSt at 210°F, a viscosity of from about 9 to about 12.5 cSt at 100°F, and a viscosity of less than about 2000 cSt at -65°F, with the proviso that the viscosity index improver is not a poly(alkyl acrylate) ester
 - 25 wherein the hydraulic fluid is free of dialkyl aryl phosphate and alkyl diaryl phosphate components.
- In a preferred embodiment, the aircraft hydraulic fluid described above further comprises from about 0.1 to about 4 weight percent, based 30 on the total weight of the hydraulic fluid, of a trialkyl phosphate wherein

-- 9 --

each alkyl group of the trialkyl phosphate is independently a straight or branched chain alkyl group of from 1 to 3 carbon atoms.

In still another of its composition aspects, this invention is directed to an aircraft hydraulic fluid comprising

- 5 (a) from about 60 to 90 weight percent, based on the total weight of the fluid, of tributyl phosphate, and from about 5 to 30 weight percent, based on the total weight of the fluid, of a second component selected from the group consisting of triaryl phosphate, a mixture of triaryl phosphate and a linear polyoxyalkylene material, and a linear polyoxyalkylene material
10 which basestock is free of dialkyl aryl phosphate and alkyl diaryl phosphate wherein each of the aryl groups of the triarylphosphate is independently phenyl or alkyl substituted phenyl having from 7 to 20 carbon atoms and still further wherein the linear polyoxyalkylene material is of the formula



wherein R^4 and R^6 are independently selected from the group consisting of hydrogen and hydrocarbyl groups of from 1 to about 30 carbon atoms, R^5 is selected from the group consisting of hydrogen and methyl, and n is an integer such that the number average molecular weight of the polymer is from about 300 to about 1000;

- 20 (b) from about 4 to about 10 weight percent, based on the total weight of the hydraulic fluid, of an acid scavenger selected from the group consisting of 7-oxabicyclo[4.1.0]heptane-3-carboxylic acid, 2-ethylhexyl ester and 7-oxabicyclo[4.1.0]heptane-3,4-dicarboxylic acid, di(*iso*-butyl) ester,

25 (c) from about 0.01 to about 0.1 weight percent, based on the total weight of the hydraulic fluid, of an anti-erosion agent which is a salt of perfluorocyclohexyl sulfonate,

- 30 (d) from about 0.5 to about 3 weight percent, based on the total weight of the hydraulic fluid, of an anti-oxidant or mixture of anti-oxidants,

-- 10 --

(e) from about 0.001 to about 1 weight percent, based on the total weight of the hydraulic fluid, of a rust inhibitor or mixture of rust inhibitors, and

(f) from about 1 to 8 weight percent, based on the total weight of
5 the hydraulic fluid, of a viscosity index improver effective in reducing the effect of temperature on viscosity on the fluid by providing for a hydraulic fluid composition containing the VI improver which has a viscosity of from about 3 to about 4 cSt at 210°F, a viscosity of from about 9 to about 12.5 cSt at 100°F, and a viscosity of less than about 2000 cSt at -65°F, with the
10 proviso that the viscosity index improver is not a poly(alkyl acrylate) ester wherein the hydraulic fluid is free of dialkyl aryl phosphate and alkyl diaryl phosphate components.

In a preferred embodiment, the basestock composition employs from about 8 to about 25 weight percent, based on the weight of the basestock,
15 of a linear polyoxypropylene or polyoxyethylene material.

In still another preferred embodiment, the rust inhibitor comprises an overbased calcium or potassium phenate or a sulfurized calcium or potassium phenate.

In one of its method aspects, this invention is directed to a method
20 for reducing electrodeposited solids during operation of an aircraft hydraulic system which method comprises:

- (a) selecting a hydraulic fluid as described above;
- (b) incorporating the selected hydraulic fluid to the aircraft hydraulic system; and
- 25 (c) operating the hydraulic system.

DETAILED DESCRIPTION OF THE INVENTION

This invention is directed to aircraft hydraulic fluid compositions comprising a specific combination of an organic phosphate ester basestock, an acid scavenging agent, an anti-erosion agent and a viscosity index improver. The compositions described herein are conventionally prepared
30

-- 11 --

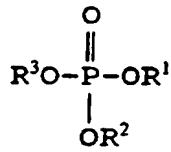
by blending the components of the composition together until homogeneous. The blending process may be conducted as a single step process where all of the components are combined and then blended or may be conducted as a multi-step process where two or more of the components 5 are combined and blended and additional components are added to the blended mixture and the resulting mixture further blended.

Organic Phosphate Ester Basestock

The hydraulic fluid composition of this invention comprises, in one embodiment, from about 60 to about 90 weight percent, based on the total 10 weight of the composition, of an organic phosphate ester basestock. This basestock, in turn, comprises from about 60 to 95 weight percent, based on the total weight of the basestock, of a trialkyl phosphate and from about 5 to about 40 weight percent, based on the total weight of the basestock, of a second component selected from the group consisting of triaryl phosphate, 15 a mixture of triaryl phosphate and a linear polyoxyalkylene material, and a linear polyoxyalkylene material. The basestock is further characterized as being free of dialkyl aryl phosphate and alkyl diaryl phosphate.

In another embodiment, the hydraulic fluid composition of this 20 invention comprises from about 60 to 90 weight percent, based on the total weight of the fluid composition, of tributyl phosphate, and from about 5 to 30 weight percent, based on the total weight of the fluid composition, of a second component selected from the group consisting of triaryl phosphate, a mixture of triaryl phosphate and a linear polyoxyalkylene material, and a linear polyoxyalkylene material which basestock is free of dialkyl aryl 25 phosphate and alkyl diaryl phosphate.

The phosphate esters can be represented by the formula:



30

-- 12 --

wherein, for the trialkyl phosphates, each of R¹, R² and R³ is independently an alkyl group of from 1 to 12 carbon atoms. For the triaryl phosphates, each of R¹, R², and R³ is independently phenyl or alkyl substituted phenyl having from 7 to 20 carbon atoms.

5 The alkyl groups of the trialkyl phosphates include aliphatic and alicyclic groups where the aliphatic groups include straight and branched alkyl groups. Examples of trialkyl phosphate esters include, by way of example, tri-*n*-butyl phosphate, tri(*iso*-butyl) phosphate, tri(*sec*-butyl) phosphate, di(*iso*-butyl) pentyl phosphate, tri(*n*-pentyl) phosphate, tri-2-
10 ethylhexyl phosphate, and the like. Preferred trialkyl phosphates include the tributyl phosphates recited above.

Mixtures of trialkyl phosphates can be used. Preferred mixtures of trialkyl phosphates include mixtures of tri(*iso*-butyl) phosphate and tri(*n*-butyl) phosphate in a ratio of about 1:1 to about 10:1, more preferably in a
15 ratio of about 2:1 to about 3:1.

The alkyl substituted phenyl groups of the triaryl phosphates include phenyl groups having from 1 to 3 alkyl substituents wherein the alkyl groups are straight or branched chain groups of from 1 to 14 carbon atoms and further wherein each alkyl substituted phenyl group has a maximum of up to 20 carbon atoms. Examples of triaryl phosphate esters include, by way of example, tri(*iso*-propylphenyl) phosphate, tri(butylated phenyl) phosphate, tricresyl phosphate, and the like. Mixtures of triaryl phosphate can be used.

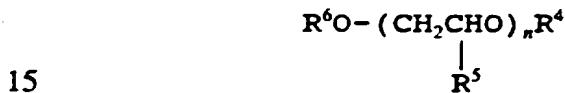
25 Particularly preferred combinations of trialkyl phosphates and triaryl phosphates include a mixture of tributyl phosphate and tri(*iso*-propylphenyl) phosphate at about a 6:1 to 8:1 ratio, preferably at about a 6:1 to 7:1 ratio (e.g., 6.7:1); and a mixture of tributyl phosphate and tri(butylated phenyl) phosphate at about a 6:1 to 7:1 ratio (e.g., 6.3:1).

In a preferred embodiment, the organic phosphate ester base stock
30 further comprises from about 0.1 to about 4 weight percent, more preferably from about 1 to 2 weight percent, based on the total weight of

-- 13 --

the hydraulic fluid, of a trialkyl phosphate wherein each alkyl group of the trialkyl phosphate is independently a straight or branched chain alkyl group of from 1 to 3 carbon atoms. Unexpectedly, it has been found that the inclusion of such a trialkyl phosphate or a mixture of such trialkyl phosphates in the organic phosphate ester base stock composition described herein provides for reduced viscosity of the hydraulic fluid at low temperatures without causing undesirable swelling of ethylene propylene seals. Preferred trialkyl phosphates useful for this purpose include trimethyl phosphate, triethyl phosphate, tri(*n*-propyl) phosphate and tri(*iso*-propyl) phosphate.

The linear polyoxyalkylene material can be characterized by the formula



wherein R⁴ and R⁶ are independently selected from the group consisting of hydrogen and hydrocarbyl groups of from 1 to about 30 carbon atoms, R⁵ is selected from the group consisting of hydrogen and methyl, and n is an integer such that the number average molecular weight of the polymer is from about 300 to about 1000. Such materials are either commercially available or can be prepared by methods known *per se* in the art. See, for example, U.S. Patent No. 4,933,485 which is incorporated herein by reference in its entirety.

Unexpectedly, it has been found that the inclusion of such linear polyoxypropylene or polyoxyethylene material in the organic phosphate ester basestock composition synergistically provides for enhanced hydrolytic stability. Additionally, the composition provides for significantly reduced titanium weight loss and hydrogen incorporation which leads to increased resistance to titanium embrittlement in high temperature exposure tests.

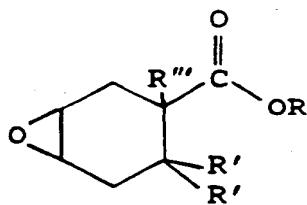
-- 14 --

As used herein, the term "hydrocarbyl" denotes an organic radical composed of carbon and hydrogen which may be aliphatic, alicyclic, aromatic or combinations thereof (e.g., arylalkyl). Preferably, the hydrocarbyl group will be relatively free of aliphatic unsaturation, i.e., 5 ethylene and acetylenic unsaturation, particularly acetylenic unsaturation.

The Acid Scavenger

The aircraft hydraulic fluid composition of this invention comprises an acid scavenger of the formula

10



15

where R is selected from the group consisting of an alkyl group of from 1 to 10 carbon atoms optionally containing from 1 to 4 ether oxygen atoms therein and cycloalkyl of from 3 to 10 carbon atoms, each R' is independently selected from the group consisting of hydrogen, alkyl of 20 from 1 to 10 carbon atoms and -C(O)OR" where R" is alkyl of from 1 to 10 carbon atoms optionally containing from 1 to 4 ether oxygen atoms therein or cycloalkyl of from 3 to 10 carbon atoms, R'' is selected from the group consisting of hydrogen, alkyl of from 1 to 10 carbons atoms and -C(O)OR" where R" is alkyl of from 1 to 10 carbon atoms optionally 25 containing from 1 to 4 ether oxygen atoms therein or cycloalkyl of from 3 to 10 carbon atoms.

Preferred acid scavengers of the above formula are the monoepoxide 7-oxabicyclo[4.1.0]heptane-3-carboxylic acid, 2-ethylhexyl ester which is disclosed in U.S. Patent No. 3,723,320, and the monoepoxide 7-oxa-30 bicyclo[4.1.0]-heptane-3,4-dicarboxylic acid, dialkyl esters [e.g., the di(isobutyl) ester]. Dialkyl esters of this monoepoxide are also disclosed in U.S.

-- 15 --

Patent No. 3,723,320. The trialkyl and tetraalkyl esters are prepared via conventional Diels-Alder reaction procedures via a suitable unsaturated trialkyl or tetraalkyl ester and a suitable 1,3-diene. The Diels-Alder reaction provides for 4 + 2 cycloaddition to provide for a cyclohexene derivative having the suitable trialkyl or tetraalkyl esters. The unsaturation in the cyclohexene is utilized to provide for epoxide formation via conventional methods.

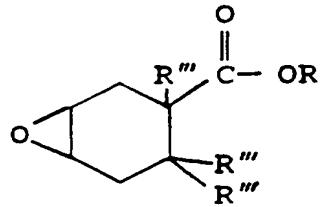
Suitable unsaturated trialkyl and tetraalkyl esters are known in the art. For example, tetraethyl ethylene tetracarboxylate is available from Fluka (Ronkonoma, NY). The alkyl groups of this tetraethyl ester can readily be exchanged via conventional techniques to provide for other esters as defined above.

The use of such di-, tri- and tetraalkyl esters of this monoepoxide unexpectedly provide for enhanced seal compatibility for the formulation of this invention as well as with conventional formulations employing conventional trihydrocarbyl phosphate basestocks with the ethylene propylene seals used in aircraft hydraulic systems.

Accordingly, in another of its method aspects, this invention is directed to a method for reducing the swelling of ethylene propylene seals in an aircraft hydraulic system due to contact of said seals with an aircraft hydraulic fluid composition containing 7-oxabicyclo-[4.1.0]heptane-3-carboxylic acid, 2-ethylhexyl ester as the acid scavenger which method comprises:

(a) replacing at least a portion of the 7-oxabicyclo-[4.1.0]heptane-3-carboxylic acid, 2-ethylhexyl ester acid scavenger with an acid scavenger of the formula:

30



-- 16 --

where R is selected from the group consisting of an alkyl group of from 1 to 10 carbon atoms optionally containing from 1 to 4 ether oxygen atoms therein and cycloalkyl of from 3 to 10 carbon atoms, each R'' is independently selected from the group consisting of hydrogen, alkyl of from 1 to 10 carbons atoms and -C(O)OR where R is as defined above, with the proviso that at least one of R'' is -C(O)OR, and

5 (b) operating the aircraft hydraulic system with the hydraulic fluid produced in (a) above.

Preferably, at least 20%, and more preferably from about 20% to
10 about 100% of the 7-oxabicyclo-[4.1.0]heptane-3-carboxylic acid, 2-ethylhexyl ester acid scavenger is replaced by the diester acid scavenger described above.

The acid scavenger, whether as the mono-, di-, tri-, or tetraester, is employed in an amount effective in scavenging the acid generated as partial
15 esters of phosphoric acid during operation of the power transmission mechanisms of an aircraft and is preferably employed at from about 4 to about 10 weight percent, based on the total weight of the hydraulic fluid composition and more preferably from about 5 to about 9 weight percent and still more preferably from about 6 to about 8 weight percent.

20

The Anti-Erosion Agent

The aircraft hydraulic fluid composition described herein comprises as the anti-erosion agent an alkali metal salt, and preferably the potassium salt, of perfluoroalkyl or perfluorocycloalkyl sulfonate which are disclosed in U.S. Patent No. 3,679,587. Such perfluoroalkyl and perfluorocyclo-
25 alkyl sulfonates preferably encompass alkyl groups of from 1 to 10 carbon atoms and cycloalkyl groups of from 3 to 10 carbon atoms. The anti-erosion agent is employed in an amount effective to inhibit erosion in the power transmission mechanisms of an aircraft and, preferably, is employed in an amount of from about 0.01 to about 0.1 weight percent, based on the
30 total weight of the hydraulic fluid composition and more preferably from

-- 17 --

about 0.025 to about 0.075 weight percent. Mixtures of such anti-erosion agents can be used.

Viscosity Index Improver

The hydraulic fluid composition described herein contains a 5 polymeric viscosity index (VI) improver to limit the effect of temperature on viscosity. The VI improvers are either non-dispersant or dispersant VI improvers which are well known in the art. Preferred VI improvers include poly(alkyl methacrylate) esters of the type disclosed in U.S. Patent No. 3,718,596 which are commercially available from Rohm & Haas, 10 Spring House, PA. Such esters typically having a molecular weight range of from about 50,000 to about 1,500,000 and preferably from about 50,000 to 250,000. Preferred VI improvers include those having a molecular weight peak at about 70,000 to 100,000 (e.g., about 85,000 or 90,000 to 100,000). A preferred VI improver is a poly(alkyl methacrylate) ester 15 sold under the tradename PA 7570 by Rohm & Haas. Mixtures of VI improvers can also be used.

The VI improver is employed in the hydraulic fluids described herein to reduce the effect of temperature on the viscosity of the fluid. VI improvers suitable for use herein are those which reduces the effect of 20 temperature on viscosity of the fluid by providing for a hydraulic fluid composition containing the VI improver which has a viscosity of from about 3 to about 4 cSt at 210°F, a viscosity of from about 9 to about 12.5 cSt at 100°F, and a viscosity of less than about 2000 cSt at -65°F. This last property is particularly significant since at high elevations extremely 25 low temperatures are encountered and, accordingly, OEM specifications require a viscosity of less than 2000 cST at -65°F.

Unexpectedly, it has been found that poly(alkyl acrylate) esters, such as those described in U.S. Patent No. 3,718,596, typically fail to adequately reduce the effect of temperature on viscosity when used in the 30 hydraulic fluids described herein. Specifically, hydraulic fluid

-- 18 --

compositions formulated with a poly(alkyl acrylate) ester generally have an unacceptably high viscosity at low temperatures (e.g., a viscosity greater than 2000 cSt at -65°F). Likewise, as shown in the examples below, still other viscosity index improvers also fail to provide adequate viscosity at 5 low temperatures.

A test to determine the usefulness of a candidate VI improver in the compositions described herein can be conducted simply by measuring the viscosity of the hydraulic fluid composition comprising this candidate VI improver in ASTM test D445 at several different temperatures (i.e., -65°F, 10 100°F and 210°F).

The VI improver is employed in an amount effective to reduce the effect of temperature on viscosity, preferably from about 1 to about 8 weight percent, more preferably from about 2 to about 8 weight percent, and still more preferably from about 3 to about 5 weight percent based on 15 the total weight of the hydraulic fluid composition. In one embodiment, the VI improver is formulated with a portion of the trialkyl phosphate basestock, typically as a 1:1 mixture.

Anti-oxidant

In a preferred embodiment, the hydraulic fluid composition 20 described herein contains a conventional anti-oxidant or mixture of anti-oxidants ("anti-oxidant"). Suitable anti-oxidants include phenolic anti-oxidants, such as 2,6-di-tertiary-butyl-*p*-cresol and tetrakis [methylene (3,5-di-*t*-butyl-4-hydroxyhydrocinnamate)]methane sold under the tradename Irganox® 1010 (Ciba-Geigy); amine anti-oxidants, including diarylamines 25 such as phenyl- α -naphthylamine or alkylphenyl- α -naphthylamine, or the reaction product of N-phenylbenzylamine with 2,4,4-trimethylpentene sold under the tradename Irganox® L-57 (Ciba-Geigy), diphenylamine, di(octylphenyl)amine sold under the tradename Vanlube® 81, ditoylamine, phenyl tolyamine, 4,4'-diaminodiphenylamine, di-*p*-methoxydiphenylamine, 30 or 4-cyclohexylaminodiphenylamine. Still other suitable anti-oxidants

-- 19 --

include aminophenols such as N-butylaminophenol, N-methyl-N-amylaminophenol and N-*iso*-octyl-p-aminophenol as well as mixtures of any such conventional anti-oxidants.

A preferred mixture of such anti-oxidants being 2,6-di-tertiary-butyl-*p*-cresol and di(octylphenyl)amine (e.g., a 1:1 mixture). Another preferred mixture of anti-oxidants is 2,6-di-tertiary-butyl-*p*-cresol, di(octylphenyl)amine and 6-methyl-2,4-bis[(octylthio)-methyl]-phenol (e.g., a 1:2:4 mixture) which mixture is particularly useful with basestocks comprising tri(*iso*-butyl) phosphate. Still another preferred mixture of anti-oxidants is 2,6-di-*t*-butyl-*p*-cresol, di(octylphenyl)amine and tetrakis [methylene(3,5-di-*t*-butyl-4-hydroxyhydrocinnamate)]methane (Irganox® 1010) (e.g., a 1:2:3 mixture).

The anti-oxidant is employed in an amount effective to inhibit oxidation of the hydraulic fluid, preferably, from about 0.5 to about 3 weight percent, more preferably from about 0.5 to 2 weight percent and still more preferably at about 1.25 to 1.75 weight percent based on the total weight of the hydraulic fluid composition.

Rust Inhibitor

In a preferred embodiment, the hydraulic fluid compositions described herein contain a rust inhibitor. Suitable rust inhibitors include, by way of example only, calcium dinonylnaphthalene sulfonate, a Group I or Group II metal overbased and/or sulfurized phenate, and a compound of the formula set forth below:



where R⁷ is selected from the group consisting of alkyl of from 1 to 40 carbon atoms, alkenyl of from 3 to 40 carbon atoms, -COOR⁸ and -CH₂CH₂N[CH₂CH(R⁹)OH]₂, where R⁸ is alkyl of from 1 to 40 carbon atoms, and wherein each R⁹ is independently selected from the group

-- 20 --

consisting of hydrogen and methyl, including N,N,N',N' tetrakis (2-hydroxypropyl) ethylene diamine and N,N-bis(2-hydroxyethyl)taallowamine sold under the tradename Ethomeen® T/12, mixtures of such inhibitors, and the like.

5 The term "alkenyl" as used herein refers to a straight or branched chain aliphatic radical having one or more olefinic double bonds, such as an oleyl group.

The Group I and Group II metal overbased and/or sulfurized phenates preferably are either sulfurized Group I or Group II metal phenates (without CO₂ added) having a Total Base Number (TBN) of from greater than 0 to about 200 or a Group I or Group II metal overbased sulfurized phenate having a TBN of from 75 to 400 prepared by the addition of carbon dioxide during the preparation of the phenate. More preferably, the metal phenate is a potassium or calcium phenate.

10 Additionally, the phenate advantageously modifies the pH to provide enhanced hydrolytic stability.

Each of these components are either commercially available or can be prepared by art recognized methods. For example, Group II metal overbased sulfurized phenates are commercially available from Chevron Chemical Company, San Ramon, California under the tradename OLOA® including, OLOA 219®, OLOA 216Q® and the like and are described by Campbell, U.S. Patent No. 5,318,710, and by MacKinnon, U.S. Patent No. 4,206,067. Likewise, N,N,N',N' tetrakis (2-hydroxy-propyl) ethylene diamine is disclosed by MacKinnon, U.S. Patent No. 4,324,674. The disclosures of each of these patents is incorporated herein in their entirety.

20 The rust inhibitor is employed in an amount effective to inhibit the formation of rust, preferably from about 0.001 to about 1 weight percent, more preferably about 0.01 to about 0.5 weight percent, and still more preferably at about 0.02 to about 0.1 weight percent based on the total

25 weight of the hydraulic fluid composition. In a preferred embodiment, the rust inhibitor comprises a mixture of N,N,N',N' tetrakis (2-hydroxypropyl)

-- 21 --

ethylene diamine and a Group II metal overbased phenate (e.g., a 5:1 mixture). In another preferred embodiment, the rust inhibitor comprises a mixture of N,N-bis(2-hydroxyethyl)taallowamine (Ethomeen® T/12) and a Group II metal overbased sulfurized phenate (e.g., a 5:1 mixture).

5

Other Additives

The hydraulic fluid composition described herein can optionally contain further conventional additives such as copper corrosion inhibitors, anti-foaming agents, dyes, etc.

10

The hydraulic fluid compositions described herein are useful in aircraft where they operate as a power transmission medium.

The following examples illustrate this invention.

EXAMPLES

Unless otherwise stated, all percents recited in the examples are 15 percents by weight.

Example 1

The purpose of this example is to demonstrate that the components employed in the compositions of this invention are compatible and synergistic with each other as evidenced by the performance characteristics 20 of the hydraulic fluid. Specifically, Formulation 1, a formulation of this invention, was prepared by blending the following components:

-- 22 --

FORMULATION 1

	<u>Component</u>	<u>Amount</u>
	trialkyl phosphate ¹	73.5 %
	tri(<i>iso</i> -propylphenyl) phosphate	10.5 %
5	7-oxabicyclo[4.1.0]heptane-3-carboxylic acid, 2-ethylhexyl ester	5.7%
	potassium perfluorocyclohexyl sulfonate	0.06%
	VI improver ²	8.7%
10	anti-oxidant ³	1.5%
	rust inhibitor ⁴	0.06%
	¹ a mixture of tri(<i>iso</i> -butyl) phosphate, tri(<i>n</i> -butyl) phosphate and triethyl phosphate (2.6:1:0.075)	
15	² a poly(alkyl methacrylate) in tributyl phosphate (1:1), available from Rohm & Haas, Philadelphia, PA, under the tradename PA 7570	
	³ a mixture of 2,6-di-tertiary-butyl- <i>p</i> -cresol, di(octylphenyl)amine and tetrakis [methylene(3,5-di- <i>t</i> -butyl-4-hydroxyhydrocinnamate)]methane (1:2:3)	
20	⁴ a mixture of N,N-bis(2-hydroxyethyl)tallowamine and a Group II metal overbased sulfurized phenate (5:1)	

The above formulation was tested for performance and was determined to increase hydrolytic stability by more than 50% as compared to a commercial aircraft hydraulic fluid and to have >500% reduction in erosion induced leakage under stressed conditions as compared to the same commercial aircraft hydraulic fluid.

-- 23 --

Example 2

The purpose of this example is to demonstrate that different viscosity index improvers do not reduce the effect of temperature on the viscosity of hydraulic fluids because at 210°F, these compositions provided acceptable viscosities only at unacceptable concentrations of VI improvers.

Specifically, three different VI improvers were used at different concentrations to determine the suitability of the VI improvers in controlling the effect of temperature on viscosity in hydraulic fluids using a mixture of tri(iso-butyl) phosphate/Durad base stocks. Durad 150 (available from FMC Corporation, Princeton, New Jersey, USA) was used at 9.9% in the first two examples whereas Durad 220B (available from FMC Corporation Princeton, New Jersey, USA) was used at 7.5% in the third example. The tri(iso-butyl) phosphate concentration ranged from 75.1 to 80.1%. Base stocks only were used for this study.

The first VI improver was referred to as "HPC 3251" which is a more shear stable polyalkylacrylate available from Royal Lubricants Company Inc., East Hanover, New Jersey, USA; the second VI improver was PA 6538, a polyalkylmethacrylate available from Rohm & Haas, Spring House, Pennsylvania, USA; and the third VI improver was PRS available from Rohm & Haas (Spring House, Pennsylvania, USA). The viscosity of these formulations was tested at 100°C (212°F). At this temperature, each of these formulations required a concentration of VI improver of greater than 9 weight percent to achieve a viscosity of from 3-4 cSt. However, the use of such large amounts of VI improvers will have a deleterious effect on the viscosity of the formulation at -65° such that, at this temperature, the formulation would be too viscous. Accordingly, these VI improvers are unacceptable for use in the claimed invention.

Example 3

The purpose of this example illustrates how a hydraulic fluid composition comprising a linear polyoxyalkylene material could be

-- 24 --

formulated for use in the formulations of this invention. Specifically, Formulation 2, a formulation of this invention, could be prepared by blending the following components:

FORMULATION 2

	<u>Component</u>	<u>Amount</u>
5	tributyl phosphate	65.5%
10	poly(oxypropylene) ¹	21.8%
	7-oxabicyclo[4.1.0]heptane-3-carboxylic acid, 2-ethylhexyl ester	6%
15	potassium perfluorocyclohexyl sulfonate	0.05%
	VI improver	5.5%
	anti-oxidant	1%
	rust inhibitor	0.1%

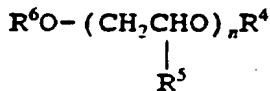
¹ available from Union Carbide, Danbury, CT, under the tradename LB-135™

It is contemplated that the above formulation, when tested for performance, would demonstrate enhanced hydrolytic stability, decreased titanium metal weight loss, and a reduction in hydrogen incorporation into the titanium as compared to a commercial aircraft hydraulic fluid. Hydrogen incorporation relates directly to titanium embrittlement with higher hydrogen incorporation correlating to higher titanium embrittlement.

-- 25 --

WHAT IS CLAIMED IS:

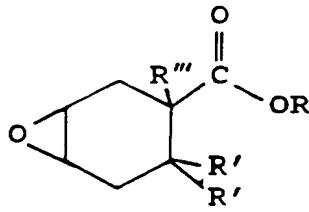
1. An aircraft hydraulic fluid comprising:
 - (a) from about 60 to about 90 weight percent, based on the total weight of the fluid, of an organic phosphate ester basestock wherein said organic phosphate ester basestock comprises from about 60 to 95 weight percent, based on the weight of the basestock, of a trialkyl phosphate wherein each of the alkyl groups thereof is independently from 1 to 12 carbon atoms and from about 5 to about 40 weight percent, based on the weight of the basestock, of a second component selected from the group consisting of a triaryl phosphate, a mixture of a triaryl phosphate and a linear polyoxyalkylene material, and a linear polyoxyalkylene material which basestock is free of dialkyl aryl phosphate and alkyl diaryl phosphate wherein each of the aryl groups of the triarylphosphate is independently phenyl or alkyl substituted phenyl having from 7 to 20 carbon atoms and still further wherein the linear polyoxyalkylene material is of the formula



wherein R^4 and R^6 are independently selected from the group consisting of hydrogen and hydrocarbyl groups of from 1 to about 30 carbon atoms, R^5 is selected from the group consisting of hydrogen and methyl, and n is an integer such that the number average molecular weight of the polymer is from about 300 to about 1000;

- (b) from about 4 to about 10 weight percent, based on the total weight of the hydraulic fluid, of an acid scavenger of the formula

30



-- 26 --

- where R is selected from the group consisting of an alkyl group of from 1 to 10 carbon atoms optionally containing from 1 to 4 ether oxygen atoms therein and cycloalkyl of from 3 to 10 carbon atoms, each R' is independently selected from the group consisting of hydrogen, alkyl of from 1 to 10 carbon atoms, and -C(O)OR" where R" is alkyl of from 1 to 10 carbon atoms optionally containing from 1 to 4 ether oxygen atoms therein or cycloalkyl of from 3 to 10 carbon atoms, and R"" is selected from the group consisting of hydrogen, alkyl of from 1 to 10 carbons atoms and -C(O)OR" where R" is alkyl of from 1 to 10 carbon atoms optionally containing from 1 to 4 ether oxygen atoms therein or cycloalkyl of from 3 to 10 carbon atoms;
- (c) from about 0.01 to about 0.1 weight percent, based on the total weight of the hydraulic fluid, of an anti-erosion agent which is a salt of perfluoroalkyl sulfonate or a perfluorocycloalkyl sulfonate wherein alkyl is alkyl of from 1 to 10 carbon atoms and cycloalkyl is cycloalkyl of from 3 to 10 carbon atoms; and
- (d) and from about 1 to about 8 weight percent of a viscosity index improver effective in reducing the effect of temperature on viscosity by providing for a hydraulic fluid composition containing the VI improver which has a viscosity of from about 3 to about 4 cSt at 210°F, a viscosity of from about 9 to about 12.5 cSt at 100°F, and a viscosity of less than about 2000 cSt at -65°F with the proviso that the viscosity index improver is not a poly(alkyl acrylate) ester.

2. The aircraft hydraulic fluid of Claim 1 which further comprises
- (e) an effective amount of an anti-oxidant or mixture of anti-oxidants to inhibit oxidation of the hydraulic fluid,
- (f) an effective amount of a rust inhibitor or mixture of rust inhibitors.

-- 27 --

3. The aircraft hydraulic fluid of Claim 2 wherein the anti-oxidant is a mixture of 2,6-di-tertiary-butyl-*p*-cresol, di(octylphenyl)amine and tetrakis [methylene(3,5-di-*t*-butyl-4-hydroxyhydrocinnamate)]-methane.
4. The aircraft hydraulic fluid of Claim 2 wherein the rust inhibitor 5 is a mixture of N,N-bis(2-hydroxyethyl)tallowamine and a Group I or Group II metal sulfurized and/or overbased phenate.
5. The aircraft hydraulic fluid of Claim 1 wherein the second component of said basestock composition is triaryl phosphate.
6. The aircraft hydraulic fluid of Claim 1 wherein the 10 second component of said basestock composition is a linear polyoxyalkylene material.
7. The aircraft hydraulic fluid of Claim 1 wherein the second component of said basestock composition is a mixture of triaryl phosphate and a linear polyoxyalkylene material.
- 15 8. The aircraft hydraulic fluid of Claim 1 wherein the acid scavenger is selected from the group consisting of 7-oxabicyclo[4.1.0]heptane-3-carboxylic acid, 2-ethylhexyl ester and 7-oxabicyclo[4.1.0]heptane-3,4-dicarboxylic acid, di(*iso*-butyl) ester.
9. The aircraft hydraulic fluid of Claim 1 wherein the anti-erosion 20 agent is the potassium salt of perfluorocyclohexyl sulfonate.
10. The aircraft hydraulic fluid of Claim 1 wherein the viscosity index improver is a poly(alkyl methacrylate) ester.

-- 28 --

11. An aircraft hydraulic fluid comprising

(a) from about 70 to 80 weight percent, based on the total weight of the fluid, of tributyl phosphate, and from about 8 to 14 weight percent, based on the total weight of the fluid, of tri(*iso*-propylphenyl)phosphate,

5 (b) from about 4.5 to about 7.5 weight percent, based on the total weight of the hydraulic fluid, of an acid scavenger which is the monoepoxide 7-oxabicyclo[4.1.0]heptane-3-carboxylic acid, 2-ethylhexyl ester,

10 (c) from about 0.01 to about 0.1 weight percent, based on the total weight of the hydraulic fluid, of an anti-erosion agent which is a salt of perfluorocyclohexyl sulfonate,

(d) from about 0.5 to about 2 weight percent, based on the total weight of the hydraulic fluid, of an anti-oxidant or mixture of anti-oxidants,

15 (e) from about 0.01 to about 0.5 weight percent, based on the total weight of the hydraulic fluid, of a rust inhibitor or mixture of rust inhibitors, and

(f) from about 1 to 8 weight percent, based on the total weight of the hydraulic fluid, of a viscosity index improver effective in reducing the effect of temperature on viscosity by providing for a hydraulic fluid composition containing the VI improver which has a viscosity of from about 3 to about 4 cSt at 210°F, a viscosity of from about 9 to about 12.5 cSt at 100°F, and a viscosity of less than about 2000 cSt at -65°F with the proviso that the viscosity index improver is not a poly(alkyl acrylate) ester,

25 wherein the hydraulic fluid is free of dialkyl aryl phosphate and alkyl diaryl phosphate components.

12. The aircraft hydraulic fluid according to Claim 11 wherein the tributyl phosphate comprises a mixture of tri(*iso*-butyl) phosphate and tri(*n*-butyl) phosphate.

-- 29 --

13. The aircraft hydraulic fluid according to Claim 12 which further comprises from about 0.1 to about 4 weight percent, based on the total weight of the hydraulic fluid, of a trialkyl phosphate wherein each alkyl group of the trialkyl phosphate is independently a straight or branched chain alkyl group of from 1 to 3 carbon atoms.

14. The aircraft hydraulic fluid according to Claim 13 wherein the trialkyl phosphate is triethyl phosphate.

15. The aircraft hydraulic fluid according to Claim 14 wherein the
anti-oxidant is a mixture of 2,6-di-tertiary-butyl-*p*-cresol,
10 di(octylphenyl)amine and tetrakis [methylene(3,5-di-*t*-butyl-4-
hydroxyhydrocinnamate)]methane.

16. The aircraft hydraulic fluid according to Claim 15 wherein the rust inhibitor comprises a compound of the formula:

$$15 \quad R^7N[CH_2CH(R^9)OH],$$

where R⁷ is selected from the group consisting of alkyl of from 1 to 40 carbon atoms, alkenyl of from 3 to 40 carbon atoms, -COOR⁸ and -CH₂CH₂N[CH₂CH(R⁹)OH]₂ where R⁸ is alkyl of from 1 to 40 carbon atoms and wherein each R⁹ is independently selected from the group consisting of hydrogen and methyl.

17. The aircraft hydraulic fluid according to Claim 16 wherein the rust inhibitor comprises N,N-bis(2-hydroxyethyl)tallowamine.

18. The aircraft hydraulic fluid according to Claim 17 wherein the
rust inhibitor further comprises a Group I or Group II metal sulfurized
and/or overbased phenate.

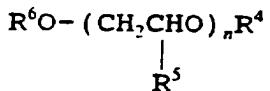
-- 30 --

19. The aircraft hydraulic fluid according to Claim 18 wherein the Group II metal sulfurized phenate is a calcium or potassium sulfurized phenate.

20. The aircraft hydraulic fluid according to Claim 19 wherein the viscosity index improver is a poly(alkyl methacrylate) ester.

21. An aircraft hydraulic fluid comprising

(a) from about 60 to 90 weight percent, based on the total weight of the fluid, of tributyl phosphate, and from about 5 to 30 weight percent, based on the total weight of the fluid, of a second component selected from the group consisting of triaryl phosphate, a mixture of triaryl phosphate and a linear polyoxyalkylene material, and a linear polyoxyalkylene material which basestock is free of dialkyl aryl phosphate and alkyl diaryl phosphate wherein each of the aryl groups of the triarylphosphate is independently phenyl or alkyl substituted phenyl having from 7 to 20 carbon atoms and still further wherein the linear polyoxyalkylene material is of the formula



wherein R^4 and R^6 are independently selected from the group consisting of hydrogen and hydrocarbyl groups of from 1 to about 30 carbon atoms, R^5 is selected from the group consisting of hydrogen and methyl, and n is an integer such that the number average molecular weight of the polymer is from about 300 to about 1000;

(b) from about 4 to about 10 weight percent, based on the total weight of the hydraulic fluid, of an acid scavenger selected from the group consisting of 7-oxabicyclo[4.1.0]heptane-3-carboxylic acid, 2-ethylhexyl ester and 7-oxabicyclo[4.1.0]heptane-3,4-dicarboxylic acid, di-*iso*-butyl ester,

-- 31 --

- (c) from about 0.01 to about 0.1 weight percent, based on the total weight of the hydraulic fluid, of an anti-erosion agent which is a salt of perfluorocyclohexyl sulfonate,
- (d) from about 0.5 to about 3 weight percent, based on the total weight of the hydraulic fluid, of an anti-oxidant or mixture of anti-oxidants,
- 5 (e) from about 0.001 to about 1 weight percent, based on the total weight of the hydraulic fluid, of a rust inhibitor or mixture of rust inhibitors, and
- (f) from about 1 to 8 weight percent, based on the total weight of the hydraulic fluid, of a viscosity index improver effective in reducing the effect of temperature on viscosity by providing for a hydraulic fluid composition containing the VI improver which has a viscosity of from about 3 to about 4 cSt at 210°F, a viscosity of from about 9 to about 12.5 cSt at 100°F, and a viscosity of less than about 2000 cSt at -65°F with the proviso that the viscosity index improver is not a poly(alkyl acrylate) ester,
- 10 wherein the hydraulic fluid is free of dialkyl aryl phosphate and alkyl diaryl phosphate components.
22. The aircraft hydraulic fluid according to Claim 21 wherein the tributyl phosphate comprises a mixture of tri(*iso*-butyl) phosphate and tri(*n*-butyl) phosphate.
- 20
23. The aircraft hydraulic fluid according to Claim 22 which further comprises from about 0.1 to about 4 weight percent, based on the total weight of the fluid, of a trialkyl phosphate wherein each alkyl group of the trialkyl phosphate is independently a straight or branched chain alkyl group of from 1 to 3 carbon atoms.
- 25
24. The aircraft hydraulic fluid according to Claim 23 wherein the trialkyl phosphate is triethyl phosphate.

-- 32 --

25. The aircraft hydraulic fluid according to Claim 24 wherein the anti-oxidant is a mixture of 2,6-di-tertiary-butyl-p-cresol, di(octylphenyl)amine and tetrakis [methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate)]methane.

5 26. The aircraft hydraulic fluid according to Claim 25 wherein the rust inhibitor comprises a compound of the formula:



where R^7 is selected from the group consisting of alkyl of from 1 to 40 carbon atoms, alkenyl of from 3 to 40 carbon atoms, -COOR⁸ and -CH₂CH₂N[CH₂CH(R⁹)OH]₂ where R⁸ is alkyl of from 1 to 40 carbon atoms and wherein each R⁹ is independently selected from the group consisting of hydrogen and methyl.

15 27. The aircraft hydraulic fluid according to Claim 26 wherein the rust inhibitor comprises N,N-bis(2-hydroxyethyl)tallowamine.

28. The aircraft hydraulic fluid according to Claim 27 wherein the rust inhibitor further comprises a Group I or Group II metal sulfurized and/or overbased phenate.

20 29. The aircraft hydraulic fluid according to Claim 28 wherein the Group II metal sulfurized phenate is a calcium or potassium sulfurized phenate.

30. The aircraft hydraulic fluid according to Claim 29 wherein the viscosity index improver is a poly(alkyl methacrylate) ester.

-- 33 --

31. A method for reducing electrodeposited solids during operation of an aircraft hydraulic system which method comprises:

- (a) selecting a hydraulic fluid from Claim 1;
- (b) incorporating the selected hydraulic fluid to the aircraft
5 hydraulic system; and
- (c) operating the hydraulic system.

**CORRECTED
VERSION***

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C10M 105/74, 129/18, 135/10	A1	(11) International Publication Number: WO 96/17517 (43) International Publication Date: 13 June 1996 (13.06.96)
(21) International Application Number: PCT/US95/15984		(74) Agents: FREELAND, Ralph, L., Jr. et al.; Burns, Doane, Swecker & Mathis, P.O. Box 1404, Alexandria, VA 22313-1404 (US).
(22) International Filing Date: 8 December 1995 (08.12.95)		
(30) Priority Data: 08/353,533 9 December 1994 (09.12.94) US		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, LS, MW, SD, SZ, UG).
(60) Parent Application or Grant (63) Related by Continuation US Filed on 08/353,533 (CIP) 9 December 1994 (09.12.94)		
(71) Applicant (for all designated States except US): CHEVRON U.S.A. INC. [US/US]; 555 Market Street, San Francisco, CA 94105 (US).		
(72) Inventors; and (75) Inventors/Applicants (for US only): OKAZAKI, Mark, E. [US/US]; 1256 Stirling Drive, Rodeo, CA 94572 (US). CHAN, Jim, H. [US/US]; 5331 Alhambra Valley Road, Martinez, CA 94533 (US). ABERNATHY, Susan, M. [US/US]; 166 Dunham Court, Hercules, CA 94547 (US). D'SOUZA, Adrian [CA/US]; 2008 Stratton Road, Walnut Creek, CA 94598 (US).		Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: HYDRAULIC FLUIDS FOR USE IN AIRCRAFT

(57) Abstract

Disclosed is an aircraft hydraulic fluid comprising a novel combination of additives and organic phosphate basestocks which provides excellent results in scavenging acid generated by the partial esters of phosphoric acid, in controlling erosion in the formulation and in reducing electrodeposited solids.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Larvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

HYDRAULIC FLUIDS FOR USE IN AIRCRAFT

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to novel hydraulic fluids containing a specific combination of components which combination imparts beneficial properties to the fluid, particularly when used as aircraft hydraulic fluids.

5 State of the Art

Hydraulic fluids, including those based on organic phosphate esters, are well known in the art and have been recognized for quite some time as advantageous for use in aircraft where they operate as a power transmission medium. In addition to the organic phosphate ester basestock, the aircraft 10 hydraulic fluid is conventionally formulated to include additives such as viscosity index improvers, anti-erosion agents, acid scavengers, anti-oxidants, rust inhibitors and the like so that the composition meets the needs of modern aircraft.

One problem typically encountered with aircraft hydraulic fluids is 15 that combinations of additives in a particular basestock do not always provide for the desired or expected combination of properties. For example, a combination of additives in one basestock may not perform nearly as well as in another basestock. Also, the inclusion of an additional additive into a hydraulic fluid formulation can deleteriously affect the 20 performance of one or more of the additives already employed in that formulation. The art has typically assigned some sort of incompatibility of the basestock with one or more of the additives employed in conjunction therewith or incompatibility of one additive with one or more of the other additives used in the formulation in order to explain this phenomena. In

-- 2 --

any event, formulation of suitable aircraft hydraulic fluids is an empirical exercise and the formulator typically is required to balance the properties of the formulation against the particular additives and basestocks employed.

Particular problems of concern to the formulator include the

- 5 inclusion of suitable acid scavengers, anti-erosion agents and viscosity index improvers in the aircraft hydraulic formulation. Specifically, in use, aircraft hydraulic fluids commonly become contaminated with moisture. Water enters the hydraulic system with air bled from an engine compressor stage. During operation, the moisture level in the fluid can typically range
10 from about 0.1 to about 0.5 weight percent. Water causes hydrolytic decomposition of phosphate esters to produce partial esters of phosphoric acid which can cause corrosion. In turn, corrosion can lead to the presence of metallic or other insoluble components which may result in filter clogging thereby necessitating filter replacement. The presence of metallic
15 or other insoluble components can also cause a change in the physical and chemical properties of the fluid, thereby requiring premature draining of the fluid from the system. Hydrolytic breakdown of the ester is accelerated if the water content exceeds about 0.5 weight percent and by the presence of partial esters of phosphoric acid. Accordingly, phosphate
20 ester aircraft hydraulic fluids are conventionally formulated to contain an acid scavenger which neutralizes partial esters of phosphoric acid released by this hydrolytic breakdown.

Similarly, an anti-erosion agent is incorporated into the aircraft hydraulic fluid to counteract erosive conditions typically occurring in the power transmission mechanisms of the aircraft. Erosion is a form of electrochemical corrosion, more precisely referred to as zeta corrosion. The process of erosion results in the wearing of the metering edges of the hydraulic valves leading to degraded performance of the hydraulic systems. Erosion can also lead to metal contaminants, in ionic form, which reduce
30 the oxidative stability of the fluid thereby accelerating corrosion and

-- 3 --

catalytically accelerating the decomposition of the phosphate ester basestock.

Viscosity index improvers are employed to limit the effect of temperature on the viscosity of the hydraulic fluid composition.

5 Specifically, while viscosity control at both elevated and reduced temperatures is essential for the hydraulic fluid, it is critically important that viscosity control be maintained at reduced temperatures typically encountered during flights at high altitudes.

It is recognized in the art that not all combinations of phosphate ester basestocks, acid scavengers, erosion inhibitors and viscosity index improvers are compatible with each other. Accordingly, it would be particularly desirable to provide for an aircraft hydraulic fluid comprising a phosphate ester basestock and as additives therein an acid scavenger, an anti-erosion agent and a viscosity index improver that are not incompatible 10 with each other or with the basestock and which function suitably under all conditions.

This invention overcomes the problems of the prior art by providing for an aircraft hydraulic fluid comprising a novel combination of additives and organic phosphate basestocks which provides excellent results in 20 scavenging acid generated by the partial esters of phosphoric acid, in controlling erosion at the metering edges of the hydraulic servo valves, in reducing electrodeposited solids and in maintaining suitable viscosity over a wide range of temperatures. These results are particularly surprising because rather than being incompatible, the additives and basestock 25 employed in the formulation described herein are, in fact, synergistic.

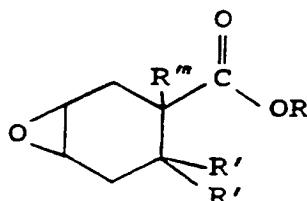
The formulation discovered by this invention comprises:

a basestock combination of from about 60 to 95 weight percent of a trialkyl phosphate and from about 5 to about 40 weight percent of a second component selected from the group consisting of a triaryl phosphate, a 30 mixture of a triaryl phosphate and a linear polyoxyalkylene material, and a

-- 4 --

linear polyoxyalkylene material which basestock is free of dialkyl aryl phosphate and alkyl diaryl phosphate,
an acid scavenger of the formula

5



10

where R is selected from the group consisting of an alkyl group of from 1 to 10 carbon atoms optionally containing from 1 to 4 ether oxygen atoms therein and cycloalkyl of from 3 to 10 carbon atoms, each R' is independently selected from the group consisting of hydrogen, alkyl of from 1 to 10 carbon atoms and -C(O)OR" where R" is alkyl of from 1 to 10 carbon atoms optionally containing from 1 to 4 ether oxygen atoms therein or cycloalkyl of from 3 to 10 carbon atoms, and R'' is selected from the group consisting of hydrogen, alkyl of from 1 to 10 carbon atoms and -C(O)OR" where R" is alkyl of from 1 to 10 carbon atoms optionally containing from 1 to 4 ether oxygen atoms therein or cycloalkyl of from 3 to 10 carbon atoms;

15

an anti-erosion agent which is a salt of perfluoroalkyl or perfluorocycloalkyl sulfonate;

20

and from about 1 to about 8 weight percent of a viscosity index improver to reduce the effect of temperature on viscosity by providing for a

25

hydraulic fluid composition containing the VI improver and having a viscosity of from about 3 to about 4 cSt at 210°F, a viscosity of from about 9 to about 12.5 cSt at 100°F, and a viscosity of less than about 2000 cSt at -65°F with the proviso that the viscosity index improver is not a poly(alkyl acrylate) ester.

30

While each of the components employed herein are similar to those heretofore disclosed for use in aircraft hydraulic fluids, the particular

-- 5 --

combination of these components is believed to be novel and unexpectedly leads to a balanced formulation providing synergistic results including, by way of example, reductions in electrodeposited solids, enhanced hydrolytic stability and/or improved erosion control while maintaining suitable 5 viscosity over a wide range of temperatures. It is understood that not all formulations of this invention will necessarily provide all of the above synergies but each formulation will provide at least one of the above synergies.

In regard to the above, the use of a phosphate basestock comprising 10 a mixture of triaryl phosphate and trialkyl phosphate in aircraft hydraulic fluids is disclosed in U.S. Patent No. 5,035,824; the use of alkali (e.g., potassium) perfluoroalkyl or perfluorocycloalkyl sulfonate as an anti-erosion agent in aircraft hydraulic fluids is disclosed in U.S. Patent No. 3,679,587; and the use of certain epoxides of the formula described above 15 in aircraft hydraulic fluids is disclosed in U.S. Patent No. 3,723,320. Moreover, commercially available hydraulic fluids used in aircraft and sold under the trademark Skydrol® by Monsanto Company (St. Louis, Missouri, USA) are believed to comprise a basestock having trialkyl phosphate, dialkyl aryl phosphate and alkyl diaryl phosphate components with little or 20 no triaryl phosphate as well as potassium perfluorocyclohexyl sulfonate and the monoepoxide 7-oxabicyclo[4.1.0]heptane-3-carboxylic acid, 2-ethylhexyl ester.

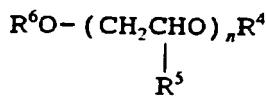
SUMMARY OF THE INVENTION

This invention is directed to an aircraft hydraulic fluid comprising a 25 novel combination of additives and organic phosphate basestocks which provides excellent results in scavenging acid generated by the partial esters of phosphoric acid, in controlling erosion in the formulation, and in reducing electrodeposited solids. These results are particularly surprising because rather than being incompatible, the additives and basestock 30 employed in the formulation described herein are, in fact, synergistic.

-- 6 --

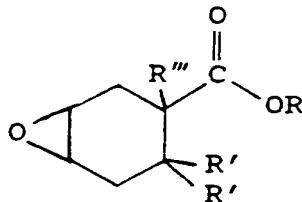
Specifically, in one of its composition aspects, this invention is directed to an aircraft hydraulic fluid comprising

- (a) from about 60 to about 90 weight percent, based on the total weight of the fluid, of an organic phosphate ester basestock wherein said organic phosphate ester basestock comprises from about 60 to 95 weight percent, based on the weight of the basestock, of a trialkyl phosphate wherein each of the alkyl groups thereof is independently from 1 to 12 carbon atoms and from about 5 to about 40 weight percent, based on the weight of the basestock, of a second component selected from the group consisting of a triaryl phosphate, a mixture of a triaryl phosphate and a linear polyoxyalkylene material, and a linear polyoxyalkylene material which basestock is free of dialkyl aryl phosphate and alkyl diaryl phosphate wherein each of the aryl groups of the triarylphosphate is independently phenyl or alkyl substituted phenyl having from 7 to 20 carbon atoms and still further wherein the linear polyoxyalkylene material is of the formula



wherein R^4 and R^6 are independently selected from the group consisting of hydrogen and hydrocarbyl groups of from 1 to about 30 carbon atoms, R^5 is selected from the group consisting of hydrogen and methyl, and n is an integer such that the number average molecular weight of the polymer is from about 300 to about 1000;

- (b) from about 4 to about 10 weight percent, based on the total weight of the hydraulic fluid, of an acid scavenger of the formula



where R is selected from the group consisting of an alkyl group of from 1 to 10 carbon atoms optionally containing from 1 to 4 ether oxygen

-- 7 --

- atoms therein and cycloalkyl of from 3 to 10 carbon atoms, each R' is independently selected from the group consisting of hydrogen, alkyl of from 1 to 10 carbon atoms and -C(O)OR" where R" is alkyl of from 1 to 10 carbon atoms optionally containing from 1 to 4 ether oxygen atoms
- 5 therein or cycloalkyl of from 3 to 10 carbon atoms, and R"" is selected from the group consisting of hydrogen, alkyl of from 1 to 10 carbons atoms and -C(O)OR" where R" is alkyl of from 1 to 10 carbon atoms optionally containing from 1 to 4 ether oxygen atoms therein or cycloalkyl of from 3 to 10 carbon atoms;
- 10 (c) from about 0.01 to about 0.1 weight percent, based on the total weight of the hydraulic fluid, of an anti-erosion agent which is a salt of perfluoroalkyl sulfonate or a perfluorocycloalkyl sulfonate wherein alkyl is alkyl of from 1 to 10 carbon atoms and cycloalkyl is cycloalkyl of from 3 to 10 carbon atoms; and
- 15 (d) from about 1 to about 8 weight percent of a viscosity index improver effective in reducing the effect of temperature on viscosity on the fluid by providing for a hydraulic fluid composition containing the VI improver which has a viscosity of from about 3 to about 4 cSt at 210°F, a viscosity of from about 9 to about 12.5 cSt at 100°F, and a viscosity of
- 20 less than about 2000 cSt at -65°F, with the proviso that the viscosity index improver is not a poly(alkyl acrylate) ester.
- In a preferred embodiment, the acid scavenger is selected from the group consisting of 7-oxabicyclo[4.1.0]heptane-3-carboxylic acid, 2-ethylhexyl ester and 7-oxabicyclo[4.1.0]heptane-3,4-dicarboxylic acid,
- 25 di(*iso*-butyl) ester.
- In another preferred embodiment, the aircraft hydraulic fluid described above further comprises
- (e) an effective amount of an anti-oxidant or mixture of anti-oxidants to inhibit oxidation of the hydraulic fluid, and
- 30 (f) an effective amount of a rust inhibitor or mixture of rust inhibitors.

-- 8 --

In another of its composition aspects, this invention is directed to an aircraft hydraulic fluid comprising

- (a) from about 70 to 80 weight percent, based on the total weight of the fluid, of tributyl phosphate, and from about 8 to 14 weight percent, 5 based on the total weight of the fluid, of tri(iso-propylphenyl)phosphate,
- (b) from about 4.5 to about 7.5 weight percent, based on the total weight of the hydraulic fluid, of an acid scavenger which is the monoepoxide 7-oxabicyclo[4.1.0]heptane-3-carboxylic acid, 2-ethylhexyl ester,
- 10 (c) from about 0.01 to about 0.1 weight percent, based on the total weight of the hydraulic fluid, of an anti-erosion agent which is a salt of perfluorocyclohexyl sulfonate,
- (d) from about 0.5 to about 2 weight percent, based on the total weight of the hydraulic fluid, of an anti-oxidant or mixture of anti-oxidants,
- 15 (e) from about 0.01 to about 0.5 weight percent, based on the total weight of the hydraulic fluid, of a rust inhibitor or mixture of rust inhibitors, and
- (f) from about 1 to about 8 weight percent, based on the total weight of the hydraulic fluid, of a viscosity index improver effective in 20 reducing the effect of temperature on viscosity on the fluid by providing for a hydraulic fluid composition containing the VI improver which has a viscosity of from about 3 to about 4 cSt at 210°F, a viscosity of from about 9 to about 12.5 cSt at 100°F, and a viscosity of less than about 2000 cSt at -65°F, with the proviso that the viscosity index improver is not a poly(alkyl acrylate) ester
- 25 wherein the hydraulic fluid is free of dialkyl aryl phosphate and alkyl diaryl phosphate components.
- In a preferred embodiment, the aircraft hydraulic fluid described above further comprises from about 0.1 to about 4 weight percent, based 30 on the total weight of the hydraulic fluid, of a trialkyl phosphate wherein

-- 9 --

each alkyl group of the trialkyl phosphate is independently a straight or branched chain alkyl group of from 1 to 3 carbon atoms.

In still another of its composition aspects, this invention is directed to an aircraft hydraulic fluid comprising

- 5 (a) from about 60 to 90 weight percent, based on the total weight of the fluid, of tributyl phosphate, and from about 5 to 30 weight percent, based on the total weight of the fluid, of a second component selected from the group consisting of triaryl phosphate, a mixture of triaryl phosphate and a linear polyoxyalkylene material, and a linear polyoxyalkylene material
10 which basestock is free of dialkyl aryl phosphate and alkyl diaryl phosphate wherein each of the aryl groups of the triarylphosphate is independently phenyl or alkyl substituted phenyl having from 7 to 20 carbon atoms and still further wherein the linear polyoxyalkylene material is of the formula



15 wherein R^4 and R^6 are independently selected from the group consisting of hydrogen and hydrocarbyl groups of from 1 to about 30 carbon atoms, R^5 is selected from the group consisting of hydrogen and methyl, and n is an integer such that the number average molecular weight of the polymer is from about 300 to about 1000;

- 20 (b) from about 4 to about 10 weight percent, based on the total weight of the hydraulic fluid, of an acid scavenger selected from the group consisting of 7-oxabicyclo[4.1.0]heptane-3-carboxylic acid, 2-ethylhexyl ester and 7-oxabicyclo[4.1.0]heptane-3,4-dicarboxylic acid, di(iso-butyl) ester,

- 25 (c) from about 0.01 to about 0.1 weight percent, based on the total weight of the hydraulic fluid, of an anti-erosion agent which is a salt of perfluorocyclohexyl sulfonate,
30 (d) from about 0.5 to about 3 weight percent, based on the total weight of the hydraulic fluid, of an anti-oxidant or mixture of anti-oxidants,

-- 10 --

(e) from about 0.001 to about 1 weight percent, based on the total weight of the hydraulic fluid, of a rust inhibitor or mixture of rust inhibitors, and

5 (f) from about 1 to 8 weight percent, based on the total weight of the hydraulic fluid, of a viscosity index improver effective in reducing the effect of temperature on viscosity on the fluid by providing for a hydraulic fluid composition containing the VI improver which has a viscosity of from about 3 to about 4 cSt at 210°F, a viscosity of from about 9 to about 12.5 cSt at 100°F, and a viscosity of less than about 2000 cSt at -65°F, with the
10 proviso that the viscosity index improver is not a poly(alkyl acrylate) ester wherein the hydraulic fluid is free of dialkyl aryl phosphate and alkyl diaryl phosphate components.

In a preferred embodiment, the basestock composition employs from about 8 to about 25 weight percent, based on the weight of the basestock,
15 of a linear polyoxypropylene or polyoxyethylene material.

In still another preferred embodiment, the rust inhibitor comprises an overbased calcium or potassium phenate or a sulfurized calcium or potassium phenate.

20 In one of its method aspects, this invention is directed to a method for reducing electrodeposited solids during operation of an aircraft hydraulic system which method comprises:

- 25 (a) selecting a hydraulic fluid as described above;
- (b) incorporating the selected hydraulic fluid to the aircraft hydraulic system; and
- (c) operating the hydraulic system.

DETAILED DESCRIPTION OF THE INVENTION

This invention is directed to aircraft hydraulic fluid compositions comprising a specific combination of an organic phosphate ester basestock, an acid scavenging agent, an anti-erosion agent and a viscosity index improver. The compositions described herein are conventionally prepared
30

-- 11 --

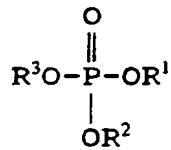
by blending the components of the composition together until homogeneous. The blending process may be conducted as a single step process where all of the components are combined and then blended or may be conducted as a multi-step process where two or more of the components 5 are combined and blended and additional components are added to the blended mixture and the resulting mixture further blended.

Organic Phosphate Ester Basestock

The hydraulic fluid composition of this invention comprises, in one embodiment, from about 60 to about 90 weight percent, based on the total 10 weight of the composition, of an organic phosphate ester basestock. This basestock, in turn, comprises from about 60 to 95 weight percent, based on the total weight of the basestock, of a trialkyl phosphate and from about 5 to about 40 weight percent, based on the total weight of the basestock, of a second component selected from the group consisting of triaryl phosphate, 15 a mixture of triaryl phosphate and a linear polyoxyalkylene material, and a linear polyoxyalkylene material. The basestock is further characterized as being free of dialkyl aryl phosphate and alkyl diaryl phosphate.

In another embodiment, the hydraulic fluid composition of this invention comprises from about 60 to 90 weight percent, based on the total 20 weight of the fluid composition, of tributyl phosphate, and from about 5 to 30 weight percent, based on the total weight of the fluid composition, of a second component selected from the group consisting of triaryl phosphate, a mixture of triaryl phosphate and a linear polyoxyalkylene material, and a linear polyoxyalkylene material which basestock is free of dialkyl aryl 25 phosphate and alkyl diaryl phosphate.

The phosphate esters can be represented by the formula:



-- 12 --

wherein, for the trialkyl phosphates, each of R¹, R² and R³ is independently an alkyl group of from 1 to 12 carbon atoms. For the triaryl phosphates, each of R¹, R², and R³ is independently phenyl or alkyl substituted phenyl having from 7 to 20 carbon atoms.

5 The alkyl groups of the trialkyl phosphates include aliphatic and alicyclic groups where the aliphatic groups include straight and branched alkyl groups. Examples of trialkyl phosphate esters include, by way of example, tri-*n*-butyl phosphate, tri(*iso*-butyl) phosphate, tri(*sec*-butyl) phosphate, di(*iso*-butyl) pentyl phosphate, tri(*n*-pentyl) phosphate, tri-2-
10 ethylhexyl phosphate, and the like. Preferred trialkyl phosphates include the tributyl phosphates recited above.

15 Mixtures of trialkyl phosphates can be used. Preferred mixtures of trialkyl phosphates include mixtures of tri(*iso*-butyl) phosphate and tri(*n*-butyl) phosphate in a ratio of about 1:1 to about 10:1, more preferably in a ratio of about 2:1 to about 3:1.

20 The alkyl substituted phenyl groups of the triaryl phosphates include phenyl groups having from 1 to 3 alkyl substituents wherein the alkyl groups are straight or branched chain groups of from 1 to 14 carbon atoms and further wherein each alkyl substituted phenyl group has a maximum of up to 20 carbon atoms. Examples of triaryl phosphate esters include, by way of example, tri(*iso*-propylphenyl) phosphate, tri(butylated phenyl) phosphate, tricresyl phosphate, and the like. Mixtures of triaryl phosphate can be used.

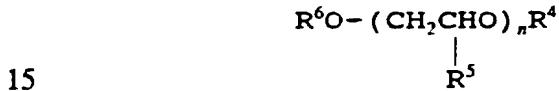
25 Particularly preferred combinations of trialkyl phosphates and triaryl phosphates include a mixture of tributyl phosphate and tri(*iso*-propylphenyl) phosphate at about a 6:1 to 8:1 ratio, preferably at about a 6:1 to 7:1 ratio (e.g., 6.7:1); and a mixture of tributyl phosphate and tri(butylated phenyl) phosphate at about a 6:1 to 7:1 ratio (e.g., 6.3:1).

30 In a preferred embodiment, the organic phosphate ester base stock further comprises from about 0.1 to about 4 weight percent, more preferably from about 1 to 2 weight percent, based on the total weight of

-- 13 --

the hydraulic fluid, of a trialkyl phosphate wherein each alkyl group of the trialkyl phosphate is independently a straight or branched chain alkyl group of from 1 to 3 carbon atoms. Unexpectedly, it has been found that the inclusion of such a trialkyl phosphate or a mixture of such trialkyl phosphates in the organic phosphate ester base stock composition described herein provides for reduced viscosity of the hydraulic fluid at low temperatures without causing undesirable swelling of ethylene propylene seals. Preferred trialkyl phosphates useful for this purpose include trimethyl phosphate, triethyl phosphate, tri(*n*-propyl) phosphate and tri(*iso*-propyl) phosphate.

The linear polyoxyalkylene material can be characterized by the formula



wherein R⁴ and R⁶ are independently selected from the group consisting of hydrogen and hydrocarbyl groups of from 1 to about 30 carbon atoms, R⁵ is selected from the group consisting of hydrogen and methyl, and n is an integer such that the number average molecular weight of the polymer is from about 300 to about 1000. Such materials are either commercially available or can be prepared by methods known *per se* in the art. See, for example, U.S. Patent No. 4,933,485 which is incorporated herein by reference in its entirety.

Unexpectedly, it has been found that the inclusion of such linear polyoxypropylene or polyoxyethylene material in the organic phosphate ester basestock composition synergistically provides for enhanced hydrolytic stability. Additionally, the composition provides for significantly reduced titanium weight loss and hydrogen incorporation which leads to increased resistance to titanium embrittlement in high temperature exposure tests.

-- 14 --

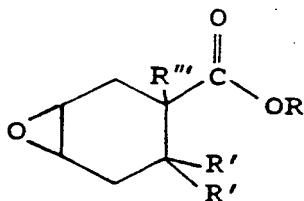
As used herein, the term "hydrocarbyl" denotes an organic radical composed of carbon and hydrogen which may be aliphatic, alicyclic, aromatic or combinations thereof (e.g., arylalkyl). Preferably, the hydrocarbyl group will be relatively free of aliphatic unsaturation, i.e., 5 ethylene and acetylenic unsaturation, particularly acetylenic unsaturation.

The Acid Scavenger

The aircraft hydraulic fluid composition of this invention comprises an acid scavenger of the formula

10

15



20

25

where R is selected from the group consisting of an alkyl group of from 1 to 10 carbon atoms optionally containing from 1 to 4 ether oxygen atoms therein and cycloalkyl of from 3 to 10 carbon atoms, each R' is independently selected from the group consisting of hydrogen, alkyl of from 1 to 10 carbon atoms and -C(O)OR" where R" is alkyl of from 1 to 10 carbon atoms optionally containing from 1 to 4 ether oxygen atoms therein or cycloalkyl of from 3 to 10 carbon atoms, R''' is selected from the group consisting of hydrogen, alkyl of from 1 to 10 carbons atoms and -C(O)OR" where R" is alkyl of from 1 to 10 carbon atoms optionally containing from 1 to 4 ether oxygen atoms therein or cycloalkyl of from 3 to 10 carbon atoms.

30

Preferred acid scavengers of the above formula are the monoepoxide 7-oxabicyclo[4.1.0]heptane-3-carboxylic acid, 2-ethylhexyl ester which is disclosed in U.S. Patent No. 3,723,320, and the monoepoxide 7-oxa-
bicyclo[4.1.0]-heptane-3,4-dicarboxylic acid, dialkyl esters [e.g., the di(iso-butyl) ester]. Dialkyl esters of this monoepoxide are also disclosed in U.S.

-- 15 --

Patent No. 3,723,320. The trialkyl and tetraalkyl esters are prepared via conventional Diels-Alder reaction procedures via a suitable unsaturated trialkyl or tetraalkyl ester and a suitable 1,3-diene. The Diels-Alder reaction provides for 4 + 2 cycloaddition to provide for a cyclohexene derivative having the suitable trialkyl or tetraalkyl esters. The unsaturation in the cyclohexene is utilized to provide for epoxide formation via conventional methods.

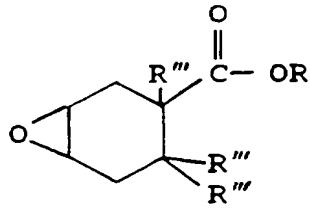
Suitable unsaturated trialkyl and tetraalkyl esters are known in the art. For example, tetraethyl ethylene tetracarboxylate is available from Fluka (Ronkonoma, NY). The alkyl groups of this tetraethyl ester can readily be exchanged via conventional techniques to provide for other esters as defined above.

The use of such di-, tri- and tetraalkyl esters of this monoepoxide unexpectedly provide for enhanced seal compatibility for the formulation of this invention as well as with conventional formulations employing conventional trihydrocarbyl phosphate basestocks with the ethylene propylene seals used in aircraft hydraulic systems.

Accordingly, in another of its method aspects, this invention is directed to a method for reducing the swelling of ethylene propylene seals in an aircraft hydraulic system due to contact of said seals with an aircraft hydraulic fluid composition containing 7-oxabicyclo-[4.1.0]heptane-3-carboxylic acid, 2-ethylhexyl ester as the acid scavenger which method comprises:

(a) replacing at least a portion of the 7-oxabicyclo-[4.1.0]heptane-3-carboxylic acid, 2-ethylhexyl ester acid scavenger with an acid scavenger of the formula:

30



-- 16 --

where R is selected from the group consisting of an alkyl group of from 1 to 10 carbon atoms optionally containing from 1 to 4 ether oxygen atoms therein and cycloalkyl of from 3 to 10 carbon atoms, each R'' is independently selected from the group consisting of hydrogen, alkyl of 5 from 1 to 10 carbons atoms and -C(O)OR where R is as defined above, with the proviso that at least one of R'' is -C(O)OR, and

(b) operating the aircraft hydraulic system with the hydraulic fluid produced in (a) above.

Preferably, at least 20%, and more preferably from about 20% to 10 about 100% of the 7-oxabicyclo-[4.1.0]heptane-3-carboxylic acid, 2-ethylhexyl ester acid scavenger is replaced by the diester acid scavenger described above.

The acid scavenger, whether as the mono-, di-, tri-, or tetraester, is employed in an amount effective in scavenging the acid generated as partial 15 esters of phosphoric acid during operation of the power transmission mechanisms of an aircraft and is preferably employed at from about 4 to about 10 weight percent, based on the total weight of the hydraulic fluid composition and more preferably from about 5 to about 9 weight percent and still more preferably from about 6 to about 8 weight percent.

20

The Anti-Erosion Agent

The aircraft hydraulic fluid composition described herein comprises as the anti-erosion agent an alkali metal salt, and preferably the potassium salt, of perfluoroalkyl or perfluorocycloalkyl sulfonate which are disclosed in U.S. Patent No. 3,679,587. Such perfluoroalkyl and perfluorocyclo- 25 alkyl sulfonates preferably encompass alkyl groups of from 1 to 10 carbon atoms and cycloalkyl groups of from 3 to 10 carbon atoms. The anti-erosion agent is employed in an amount effective to inhibit erosion in the power transmission mechanisms of an aircraft and, preferably, is employed in an amount of from about 0.01 to about 0.1 weight percent, based on the 30 total weight of the hydraulic fluid composition and more preferably from

-- 17 --

about 0.025 to about 0.075 weight percent. Mixtures of such anti-erosion agents can be used.

Viscosity Index Improver

The hydraulic fluid composition described herein contains a polymeric viscosity index (VI) improver to limit the effect of temperature on viscosity. The VI improvers are either non-dispersant or dispersant VI improvers which are well known in the art. Preferred VI improvers include poly(alkyl methacrylate) esters of the type disclosed in U.S. Patent No. 3,718,596 which are commercially available from Rohm & Haas, Spring House, PA. Such esters typically having a molecular weight range of from about 50,000 to about 1,500,000 and preferably from about 50,000 to 250,000. Preferred VI improvers include those having a molecular weight peak at about 70,000 to 100,000 (e.g., about 85,000 or 90,000 to 100,000). A preferred VI improver is a poly(alkyl methacrylate) ester sold under the tradename PA 7570 by Rohm & Haas. Mixtures of VI improvers can also be used.

The VI improver is employed in the hydraulic fluids described herein to reduce the effect of temperature on the viscosity of the fluid. VI improvers suitable for use herein are those which reduces the effect of temperature on viscosity of the fluid by providing for a hydraulic fluid composition containing the VI improver which has a viscosity of from about 3 to about 4 cSt at 210°F, a viscosity of from about 9 to about 12.5 cSt at 100°F, and a viscosity of less than about 2000 cSt at -65°F. This last property is particularly significant since at high elevations extremely low temperatures are encountered and, accordingly, OEM specifications require a viscosity of less than 2000 cST at -65°F.

Unexpectedly, it has been found that poly(alkyl acrylate) esters, such as those described in U.S. Patent No. 3,718,596, typically fail to adequately reduce the effect of temperature on viscosity when used in the hydraulic fluids described herein. Specifically, hydraulic fluid

-- 18 --

compositions formulated with a poly(alkyl acrylate) ester generally have an unacceptably high viscosity at low temperatures (e.g., a viscosity greater than 2000 cSt at -65°F). Likewise, as shown in the examples below, still other viscosity index improvers also fail to provide adequate viscosity at 5 low temperatures.

A test to determine the usefulness of a candidate VI improver in the compositions described herein can be conducted simply by measuring the viscosity of the hydraulic fluid composition comprising this candidate VI improver in ASTM test D445 at several different temperatures (i.e., -65°F, 10 100°F and 210°F).

The VI improver is employed in an amount effective to reduce the effect of temperature on viscosity, preferably from about 1 to about 8 weight percent, more preferably from about 2 to about 8 weight percent, and still more preferably from about 3 to about 5 weight percent based on 15 the total weight of the hydraulic fluid composition. In one embodiment, the VI improver is formulated with a portion of the trialkyl phosphate basestock, typically as a 1:1 mixture.

Anti-oxidant

In a preferred embodiment, the hydraulic fluid composition 20 described herein contains a conventional anti-oxidant or mixture of anti-oxidants ("anti-oxidant"). Suitable anti-oxidants include phenolic anti-oxidants, such as 2,6-di-tertiary-butyl-*p*-cresol and tetrakis [methylene (3,5-di-*t*-butyl-4-hydroxyhydrocinnamate)]methane sold under the tradename Irganox® 1010 (Ciba-Geigy); amine anti-oxidants, including diarylamines 25 such as phenyl- α -naphthylamine or alkylphenyl- α -naphthylamine, or the reaction product of N-phenylbenzylamine with 2,4,4-trimethylpentene sold under the tradename Irganox® L-57 (Ciba-Geigy), diphenylamine, di(octylphenyl)amine sold under the tradename Vanlube® 81, ditoylamine, phenyl tolylamine, 4,4'-diaminodiphenylamine, di-*p*-methoxydiphenylamine, 30 or 4-cyclohexylaminodiphenylamine. Still other suitable anti-oxidants

-- 19 --

include aminophenols such as N-butylaminophenol, N-methyl-N-
amylaminophenol and N-*iso*-octyl-*p*-aminophenol as well as mixtures of any
such conventional anti-oxidants.

A preferred mixture of such anti-oxidants being 2,6-di-tertiary-
5 butyl-*p*-cresol and di(octylphenyl)amine (e.g., a 1:1 mixture).
Another preferred mixture of anti-oxidants is 2,6-di-tertiary-butyl-*p*-cresol,
di(octylphenyl)amine and 6-methyl-2,4-bis[(octylthio)-methyl]-phenol (e.g.,
a 1:2:4 mixture) which mixture is particularly useful with basestocks
comprising tri(*iso*-butyl) phosphate. Still another preferred mixture of anti-
10 oxidants is 2,6-di-*t*-butyl-*p*-cresol, di(octylphenyl)amine and tetrakis
[methylene(3,5-di-*t*-butyl-4-hydroxyhydrocinnamate)]methane (Irganox®
1010) (e.g., a 1:2:3 mixture).

The anti-oxidant is employed in an amount effective to inhibit
oxidation of the hydraulic fluid, preferably, from about 0.5 to about 3
15 weight percent, more preferably from about 0.5 to 2 weight percent and
still more preferably at about 1.25 to 1.75 weight percent based on the total
weight of the hydraulic fluid composition.

Rust Inhibitor

In a preferred embodiment, the hydraulic fluid compositions
20 described herein contain a rust inhibitor. Suitable rust inhibitors include,
by way of example only, calcium dinonylnaphthalene sulfonate, a Group I
or Group II metal overbased and/or sulfurized phenate, and a compound of
the formula set forth below:



25 where R⁷ is selected from the group consisting of alkyl of from 1 to 40
carbon atoms, alkenyl of from 3 to 40 carbon atoms, -COOR⁸ and
-CH₂CH₂N[CH₂CH(R⁹)OH], where R⁸ is alkyl of from 1 to 40 carbon
atoms, and wherein each R⁹ is independently selected from the group

-- 20 --

consisting of hydrogen and methyl, including N,N,N',N' tetrakis (2-hydroxypropyl) ethylene diamine and N,N-bis(2-hydroxyethyl)tallowamine sold under the tradename Ethomeen® T/12, mixtures of such inhibitors, and the like.

5 The term "alkenyl" as used herein refers to a straight or branched chain aliphatic radical having one or more olefinic double bonds, such as an oleyl group.

The Group I and Group II metal overbased and/or sulfurized phenates preferably are either sulfurized Group I or Group II metal
10 phenates (without CO₂ added) having a Total Base Number (TBN) of from greater than 0 to about 200 or a Group I or Group II metal overbased sulfurized phenate having a TBN of from 75 to 400 prepared by the addition of carbon dioxide during the preparation of the phenate. More preferably, the metal phenate is a potassium or calcium phenate.
15 Additionally, the phenate advantageously modifies the pH to provide enhanced hydrolytic stability.

Each of these components are either commercially available or can be prepared by art recognized methods. For example, Group II metal overbased sulfurized phenates are commercially available from Chevron
20 Chemical Company, San Ramon, California under the tradename OLOA® including, OLOA 219®, OLOA 216Q® and the like and are described by Campbell, U.S. Patent No. 5,318,710, and by MacKinnon, U.S. Patent No. 4,206,067. Likewise, N,N,N',N' tetrakis (2-hydroxy-propyl) ethylene diamine is disclosed by MacKinnon, U.S. Patent No. 4,324,674. The disclosures of each of these patents is incorporated herein in their entirety.
25

The rust inhibitor is employed in an amount effective to inhibit the formation of rust, preferably from about 0.001 to about 1 weight percent, more preferably about 0.01 to about 0.5 weight percent, and still more preferably at about 0.02 to about 0.1 weight percent based on the total weight of the hydraulic fluid composition. In a preferred embodiment, the rust inhibitor comprises a mixture of N,N,N',N' tetrakis (2-hydroxypropyl)

-- 21 --

ethylene diamine and a Group II metal overbased phenate (e.g., a 5:1 mixture). In another preferred embodiment, the rust inhibitor comprises a mixture of N,N-bis(2-hydroxyethyl)tallowamine (Ethomeen® T/12) and a Group II metal overbased sulfurized phenate (e.g., a 5:1 mixture).

5

Other Additives

The hydraulic fluid composition described herein can optionally contain further conventional additives such as copper corrosion inhibitors, anti-foaming agents, dyes, etc.

10

Utility

The hydraulic fluid compositions described herein are useful in aircraft where they operate as a power transmission medium.

The following examples illustrate this invention.

EXAMPLES

15 Unless otherwise stated, all percents recited in the examples are percents by weight.

Example 1

The purpose of this example is to demonstrate that the components employed in the compositions of this invention are compatible and synergistic with each other as evidenced by the performance characteristics 20 of the hydraulic fluid. Specifically, Formulation 1, a formulation of this invention, was prepared by blending the following components:

-- 22 --

FORMULATION 1

	<u>Component</u>	<u>Amount</u>
	trialkyl phosphate ¹	73.5 %
	tri(<i>iso</i> -propylphenyl) phosphate	10.5 %
5	7-oxabicyclo[4.1.0]heptane-3-carboxylic acid, 2-ethylhexyl ester	5.7 %
	potassium perfluorocyclohexyl sulfonate	0.06 %
	VI improver ²	8.7 %
10	anti-oxidant ³	1.5 %
	rust inhibitor ⁴	0.06 %
	¹ a mixture of tri(<i>iso</i> -butyl) phosphate, tri(<i>n</i> -butyl) phosphate and triethyl phosphate (2.6:1:0.075)	
15	² a poly(alkyl methacrylate) in tributyl phosphate (1:1), available from Rohm & Haas, Philadelphia, PA, under the tradename PA 7570	
	³ a mixture of 2,6-di-tertiary-butyl- <i>p</i> -cresol, di(octylphenyl)amine and tetrakis [methylene(3,5-di- <i>t</i> -butyl-4-hydroxyhydrocinnamate)]methane (1:2:3)	
20	⁴ a mixture of N,N-bis(2-hydroxyethyl)tallowamine and a Group II metal overbased sulfurized phenate (5:1)	

The above formulation was tested for performance and was determined to increase hydrolytic stability by more than 50% as compared to a commercial aircraft hydraulic fluid and to have > 500% reduction in erosion induced leakage under stressed conditions as compared to the same commercial aircraft hydraulic fluid.

-- 23 --

Example 2

The purpose of this example is to demonstrate that different viscosity index improvers do not reduce the effect of temperature on the viscosity of hydraulic fluids because at 210°F, these compositions provided acceptable viscosities only at unacceptable concentrations of VI improvers.

Specifically, three different VI improvers were used at different concentrations to determine the suitability of the VI improvers in controlling the effect of temperature on viscosity in hydraulic fluids using a mixture of tri(iso-butyl) phosphate/Durad base stocks. Durad 150 (available from FMC Corporation, Princeton, New Jersey, USA) was used at 9.9% in the first two examples whereas Durad 220B (available from FMC Corporation Princeton, New Jersey, USA) was used at 7.5% in the third example. The tri(iso-butyl) phosphate concentration ranged from 75.1 to 80.1%. Base stocks only were used for this study.

The first VI improver was referred to as "HPC 3251" which is a more shear stable polyalkylacrylate available from Royal Lubricants Company Inc., East Hanover, New Jersey, USA; the second VI improver was PA 6538, a polyalkylmethacrylate available from Rohm & Haas, Spring House, Pennsylvania, USA; and the third VI improver was PRS available from Rohm & Haas (Spring House, Pennsylvania, USA). The viscosity of these formulations was tested at 100°C (212°F). At this temperature, each of these formulations required a concentration of VI improver of greater than 9 weight percent to achieve a viscosity of from 3-4 cSt. However, the use of such large amounts of VI improvers will have a deleterious effect on the viscosity of the formulation at -65° such that, at this temperature, the formulation would be too viscous. Accordingly, these VI improvers are unacceptable for use in the claimed invention.

Example 3

The purpose of this example illustrates how a hydraulic fluid composition comprising a linear polyoxyalkylene material could be

-- 24 --

formulated for use in the formulations of this invention. Specifically, Formulation 2, a formulation of this invention, could be prepared by blending the following components:

FORMULATION 2

	<u>Component</u>	<u>Amount</u>
5	tributyl phosphate	65.5%
10	poly(oxypropylene) ¹	21.8%
	7-oxabicyclo[4.1.0]heptane-3-carboxylic acid, 2-ethylhexyl ester	6%
15	potassium perfluorocyclohexyl sulfonate	0.05%
	VI improver	5.5%
	anti-oxidant	1%
	rust inhibitor	0.1%

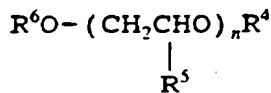
¹ available from Union Carbide, Danbury, CT, under the trademark LB-135™

It is contemplated that the above formulation, when tested for performance, would demonstrate enhanced hydrolytic stability, decreased titanium metal weight loss, and a reduction in hydrogen incorporation into the titanium as compared to a commercial aircraft hydraulic fluid. Hydrogen incorporation relates directly to titanium embrittlement with higher hydrogen incorporation correlating to higher titanium embrittlement.

-- 25 --

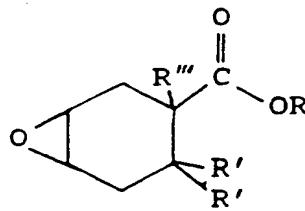
WHAT IS CLAIMED IS:

1. An aircraft hydraulic fluid comprising:
 - (a) from about 60 to about 90 weight percent, based on the total weight of the fluid, of an organic phosphate ester basestock wherein said organic phosphate ester basestock comprises from about 60 to 95 weight percent, based on the weight of the basestock, of a trialkyl phosphate wherein each of the alkyl groups thereof is independently from 1 to 12 carbon atoms and from about 5 to about 40 weight percent, based on the weight of the basestock, of a second component selected from the group consisting of a triaryl phosphate, a mixture of a triaryl phosphate and a linear polyoxyalkylene material, and a linear polyoxyalkylene material which basestock is free of dialkyl aryl phosphate and alkyl diaryl phosphate wherein each of the aryl groups of the triarylphosphate is independently phenyl or alkyl substituted phenyl having from 7 to 20 carbon atoms and still further wherein the linear polyoxyalkylene material is of the formula



wherein R^4 and R^6 are independently selected from the group consisting of hydrogen and hydrocarbyl groups of from 1 to about 30 carbon atoms, R^5 is selected from the group consisting of hydrogen and methyl, and n is an integer such that the number average molecular weight of the polymer is from about 300 to about 1000;

- 25 (b) from about 4 to about 10 weight percent, based on the total weight of the hydraulic fluid, of an acid scavenger of the formula



-- 26 --

- where R is selected from the group consisting of an alkyl group of from 1 to 10 carbon atoms optionally containing from 1 to 4 ether oxygen atoms therein and cycloalkyl of from 3 to 10 carbon atoms, each R' is independently selected from the group consisting of hydrogen, alkyl of from 1 to 10 carbon atoms, and -C(O)OR" where R" is alkyl of from 1 to 10 carbon atoms optionally containing from 1 to 4 ether oxygen atoms therein or cycloalkyl of from 3 to 10 carbon atoms, and R'' is selected from the group consisting of hydrogen, alkyl of from 1 to 10 carbons atoms and -C(O)OR" where R" is alkyl of from 1 to 10 carbon atoms optionally containing from 1 to 4 ether oxygen atoms therein or cycloalkyl of from 3 to 10 carbon atoms;
- (c) from about 0.01 to about 0.1 weight percent, based on the total weight of the hydraulic fluid, of an anti-erosion agent which is a salt of perfluoroalkyl sulfonate or a perfluorocycloalkyl sulfonate wherein alkyl is alkyl of from 1 to 10 carbon atoms and cycloalkyl is cycloalkyl of from 3 to 10 carbon atoms; and
- (d) and from about 1 to about 8 weight percent of a viscosity index improver effective in reducing the effect of temperature on viscosity by providing for a hydraulic fluid composition containing the VI improver which has a viscosity of from about 3 to about 4 cSt at 210°F, a viscosity of from about 9 to about 12.5 cSt at 100°F, and a viscosity of less than about 2000 cSt at -65°F with the proviso that the viscosity index improver is not a poly(alkyl acrylate) ester.

2. The aircraft hydraulic fluid of Claim 1 which further comprises
- (e) an effective amount of an anti-oxidant or mixture of anti-oxidants to inhibit oxidation of the hydraulic fluid,
- (f) an effective amount of a rust inhibitor or mixture of rust inhibitors.

-- 27 --

3. The aircraft hydraulic fluid of Claim 2 wherein the anti-oxidant is a mixture of 2,6-di-tertiary-butyl-*p*-cresol, di(octylphenyl)amine and tetrakis [methylene(3,5-di-*t*-butyl-4-hydroxyhydrocinnamate)]-methane.

4. The aircraft hydraulic fluid of Claim 2 wherein the rust inhibitor
5 is a mixture of N,N-bis(2-hydroxyethyl)tallowamine and a Group I or Group II metal sulfurized and/or overbased phenate.

5. The aircraft hydraulic fluid of Claim 1 wherein the second component of said basestock composition is triaryl phosphate.

6. The aircraft hydraulic fluid of Claim 1 wherein the
10 second component of said basestock composition is a linear polyoxyalkylene material.

7. The aircraft hydraulic fluid of Claim 1 wherein the second component of said basestock composition is a mixture of triaryl phosphate and a linear polyoxyalkylene material.

15 8. The aircraft hydraulic fluid of Claim 1 wherein the acid scavenger is selected from the group consisting of 7-oxabicyclo[4.1.0]heptane-3-carboxylic acid, 2-ethylhexyl ester and 7-oxabicyclo[4.1.0]heptane-3,4-dicarboxylic acid, di(*iso*-butyl) ester.

20 9. The aircraft hydraulic fluid of Claim 1 wherein the anti-erosion agent is the potassium salt of perfluorocyclohexyl sulfonate.

10. The aircraft hydraulic fluid of Claim 1 wherein the viscosity index improver is a poly(alkyl methacrylate) ester.

-- 28 --

11. An aircraft hydraulic fluid comprising

(a) from about 70 to 80 weight percent, based on the total weight of the fluid, of tributyl phosphate, and from about 8 to 14 weight percent, based on the total weight of the fluid, of tri(*iso*-propylphenyl)phosphate,

5 (b) from about 4.5 to about 7.5 weight percent, based on the total weight of the hydraulic fluid, of an acid scavenger which is the monoepoxide 7-oxabicyclo[4.1.0]heptane-3-carboxylic acid, 2-ethylhexyl ester,

10 (c) from about 0.01 to about 0.1 weight percent, based on the total weight of the hydraulic fluid, of an anti-erosion agent which is a salt of perfluorocyclohexyl sulfonate,

(d) from about 0.5 to about 2 weight percent, based on the total weight of the hydraulic fluid, of an anti-oxidant or mixture of anti-oxidants,

15 (e) from about 0.01 to about 0.5 weight percent, based on the total weight of the hydraulic fluid, of a rust inhibitor or mixture of rust inhibitors, and

(f) from about 1 to 8 weight percent, based on the total weight of the hydraulic fluid, of a viscosity index improver effective in reducing the effect of temperature on viscosity by providing for a hydraulic fluid composition containing the VI improver which has a viscosity of from about 3 to about 4 cSt at 210°F, a viscosity of from about 9 to about 12.5 cSt at 100°F, and a viscosity of less than about 2000 cSt at -65°F with the proviso that the viscosity index improver is not a poly(alkyl acrylate) ester,

25 wherein the hydraulic fluid is free of dialkyl aryl phosphate and alkyl diaryl phosphate components.

12. The aircraft hydraulic fluid according to Claim 11 wherein the tributyl phosphate comprises a mixture of tri(*iso*-butyl) phosphate and tri(*n*-butyl) phosphate.

-- 29 --

13. The aircraft hydraulic fluid according to Claim 12 which further comprises from about 0.1 to about 4 weight percent, based on the total weight of the hydraulic fluid, of a trialkyl phosphate wherein each alkyl group of the trialkyl phosphate is independently a straight or branched chain alkyl group of from 1 to 3 carbon atoms.

5

14. The aircraft hydraulic fluid according to Claim 13 wherein the trialkyl phosphate is triethyl phosphate.

10

15. The aircraft hydraulic fluid according to Claim 14 wherein the anti-oxidant is a mixture of 2,6-di-tertiary-butyl-p-cresol, di(octylphenyl)amine and tetrakis [methylene(3,5-di-*t*-butyl-4-hydroxyhydrocinnamate)]methane.

15

16. The aircraft hydraulic fluid according to Claim 15 wherein the rust inhibitor comprises a compound of the formula:

$$R^7N[CH_2CH(R^9)OH]_2$$

where R^7 is selected from the group consisting of alkyl of from 1 to 40 carbon atoms, alkenyl of from 3 to 40 carbon atoms, -COOR⁸ and -CH₂CH₂N[CH₂CH(R⁹)OH]₂, where R⁸ is alkyl of from 1 to 40 carbon atoms and wherein each R⁹ is independently selected from the group consisting of hydrogen and methyl.

20

17. The aircraft hydraulic fluid according to Claim 16 wherein the rust inhibitor comprises N,N-bis(2-hydroxyethyl)tallowamine.

18. The aircraft hydraulic fluid according to Claim 17 wherein the rust inhibitor further comprises a Group I or Group II metal sulfurized and/or overbased phenate.

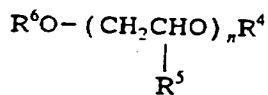
5

-- 30 --

19. The aircraft hydraulic fluid according to Claim 18 wherein the Group II metal sulfurized phenate is a calcium or potassium sulfurized phenate.

20. The aircraft hydraulic fluid according to Claim 19 wherein the viscosity index improver is a poly(alkyl methacrylate) ester.

21. An aircraft hydraulic fluid comprising
(a) from about 60 to 90 weight percent, based on the total weight of the fluid, of tributyl phosphate, and from about 5 to 30 weight percent, based on the total weight of the fluid, of a second component selected from
10 the group consisting of triaryl phosphate, a mixture of triaryl phosphate and a linear polyoxyalkylene material, and a linear polyoxyalkylene material which basestock is free of dialkyl aryl phosphate and alkyl diaryl phosphate wherein each of the aryl groups of the triarylphosphate is independently phenyl or alkyl substituted phenyl having from 7 to 20 carbon atoms and
15 still further wherein the linear polyoxyalkylene material is of the formula



wherein R⁴ and R⁶ are independently selected from the group consisting of
20 hydrogen and hydrocarbyl groups of from 1 to about 30 carbon atoms, R⁵ is selected from the group consisting of hydrogen and methyl, and n is an integer such that the number average molecular weight of the polymer is from about 300 to about 1000;

(b) from about 4 to about 10 weight percent, based on the total
25 weight of the hydraulic fluid, of an acid scavenger selected from the group consisting of 7-oxabicyclo[4.1.0]heptane-3-carboxylic acid, 2-ethylhexyl ester and 7-oxabicyclo[4.1.0]heptane-3,4-dicarboxylic acid, di-*iso*-butyl ester,

-- 31 --

(c) from about 0.01 to about 0.1 weight percent, based on the total weight of the hydraulic fluid, of an anti-erosion agent which is a salt of perfluorocyclohexyl sulfonate,

5 (d) from about 0.5 to about 3 weight percent, based on the total weight of the hydraulic fluid, of an anti-oxidant or mixture of anti-oxidants,

(e) from about 0.001 to about 1 weight percent, based on the total weight of the hydraulic fluid, of a rust inhibitor or mixture of rust inhibitors, and

10 (f) from about 1 to 8 weight percent, based on the total weight of the hydraulic fluid, of a viscosity index improver effective in reducing the effect of temperature on viscosity by providing for a hydraulic fluid composition containing the VI improver which has a viscosity of from about 3 to about 4 cSt at 210°F, a viscosity of from about 9 to about 12.5 cSt at 100°F, and a viscosity of less than about 2000 cSt at -65°F with the proviso that the viscosity index improver is not a poly(alkyl acrylate) ester, 15 wherein the hydraulic fluid is free of dialkyl aryl phosphate and alkyl diaryl phosphate components.

22. The aircraft hydraulic fluid according to Claim 21 wherein the tributyl phosphate comprises a mixture of tri(*iso*-butyl) phosphate and 20 tri(*n*-butyl) phosphate.

23. The aircraft hydraulic fluid according to Claim 22 which further comprises from about 0.1 to about 4 weight percent, based on the total weight of the fluid, of a trialkyl phosphate wherein each alkyl group of the trialkyl phosphate is independently a straight or branched chain alkyl 25 group of from 1 to 3 carbon atoms.

24. The aircraft hydraulic fluid according to Claim 23 wherein the trialkyl phosphate is triethyl phosphate.

-- 32 --

25. The aircraft hydraulic fluid according to Claim 24 wherein the anti-oxidant is a mixture of 2,6-di-tertiary-butyl-*p*-cresol, di(octylphenyl)amine and tetrakis [methylene(3,5-di-*t*-butyl-4-hydroxyhydrocinnamate)]methane.

5 26. The aircraft hydraulic fluid according to Claim 25 wherein the rust inhibitor comprises a compound of the formula:



10 where R^7 is selected from the group consisting of alkyl of from 1 to 40 carbon atoms, alkenyl of from 3 to 40 carbon atoms, -COOR⁸ and -CH₂CH₂N[CH₂CH(R⁹)OH]₂ where R⁸ is alkyl of from 1 to 40 carbon atoms and wherein each R⁹ is independently selected from the group consisting of hydrogen and methyl.

15 27. The aircraft hydraulic fluid according to Claim 26 wherein the rust inhibitor comprises N,N-bis(2-hydroxyethyl)tallowamine.

28. The aircraft hydraulic fluid according to Claim 27 wherein the rust inhibitor further comprises a Group I or Group II metal sulfurized and/or overbased phenate.

20 29. The aircraft hydraulic fluid according to Claim 28 wherein the Group II metal sulfurized phenate is a calcium or potassium sulfurized phenate.

30. The aircraft hydraulic fluid according to Claim 29 wherein the viscosity index improver is a poly(alkyl methacrylate) ester.

-- 33 --

31. A method for reducing electrodeposited solids during operation of an aircraft hydraulic system which method comprises:

- (a) selecting a hydraulic fluid from Claim 1;
- (b) incorporating the selected hydraulic fluid to the aircraft
5 hydraulic system; and
- (c) operating the hydraulic system.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/15984

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C10M 105/74, 129/18, 135/10
 US CL :252/78.5, 49.8, 52A

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/78.5, 49.8, 52A

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAS ONLINE

chemical structure search

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3,679,587 (SMITH) 25 July 1972, col. 3, line 11 - col. 4, line 36 and col. 8, line 41 - col. 9, line 9.	1-30
Y	WO 93/25641 (DEETMAN) 23 December 1993, page 4 - page 7, page 13 - page 17 and Table 1, page 22.	1-30
A	US, A, 3,723,320 (HERBER ET AL) 27 March 1973, col. 2, line 54 - col. 3, line 9, col. 4, lines 58-75 and Abstract.	9, 11-15, 20-25, 30
Y	US, A, 4,206,067 (MACKINNON) 03 June 1980, col. 5, line 57 - col. 6, line 22.	4, 16-19, 26-29
Y	US, A, 3,983,046 (SHERATTE) 28 September 1976, col. 5, line 29 - col. 8, line 59 and col. 9, line 48 - col. 14, line 62.	6, 7

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:	T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)		document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

28 MAY 1996

Date of mailing of the international search report

08 JUL 1996

Name and mailing address of the ISA/US
 Commissioner of Patents and Trademarks
 Box PCT
 Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

CHRISTINE SKANE

Telephone No. (703) 308-0661

Form PCT/ISA/210 (second sheet)(July 1992)*